References

BATTAGLIA, L. P., CORRADI, A. B. & TANI, M. E. V. (1975). *Acta Cryst.* B31, 1160–1164.

BRINTZINGER, H. & HESSE, G. (1942). *Z. Anorg. Allg. Chem.* 249, 299–307.

CHUKLANOVA, E. B., POLYNOVA, T. N., POZNYAK, A. L., DIKAREVA, L. M. & PORAI-KOSHITS, M. A. (1981). *Koord. Khim.* 7, 1729–1736; *Sov. J. Coord. Chem.* 7, 867–873.

CLEGG, W. (1981). *Acta Cryst.* A37, 22–28.

COHEN, G. H. & HOARD, J. L. (1966). *J. Am. Chem. Soc.* 88, 3228–3234.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.

KRISHNAMURTHY, M. & MORRIS, K. B. (1972). *J. Inorg. Nucl. Chem.* 34, 719–724.

KRISHNAMURTHY, M., MORRIS, K. B. & HAMBRIGHT, W. P. (1970). *J. Inorg. Nucl. Chem.* 32, 565–571.

LIND, M. D., HAMOR, M. J., HAMOR, T. A. & HOARD, J. L. (1964). *Inorg. Chem.* 3, 34–43.

NESTEROVA, YA.M., POLYNOVA, T. N. & PORAI-KOSHITS, M. A. (1975). *Koord. Khim.* 1, 966–974; *Sov. J. Coord. Chem.* 1, 819–825.

NOVOZHILOVA, N. V., POLYNOVA, T. N. & PORAI-KOSHITS, M. A. (1975). *Zh. Strukt. Khim.* 16, 865–874; *J. Struct. Chem.* 16, 796–804.

RABINOWITZ, I. N., DAVIS, F. F. & HERBER, R. H. (1966). *J. Am. Chem. Soc.* 88, 4346–4354.

SHELDRICK, G. M. (1978). *SHELXTL: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

SHIBAHARA, T., HATTORI, H. & KUROYA, H. (1984). *J. Am. Chem. Soc.* 106, 2710–2711.

SOLANS, X., FONT ALTABA, M. & GARCIA-ORICAIN, J. (1984). *Acta Cryst.* C40, 635–638.

WHITLOW, S. H. (1973). *Inorg. Chem.* 12, 2286–2289.

Structure of Calcium Chloride–Sarcosine (1/3), CaCl₂.3C₃H₇NO₂, in the Ferroelectric Phase

BY N. MISHIMA, K. ITOH AND E. NAKAMURA

Department of Materials Science, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Abstract. $M_r = 378 \cdot 3$, orthorhombic, $Pn2_1a$, $a = 9 \cdot 122$ (4), $b = 17 \cdot 408$ (4), $c = 10 \cdot 228$ (8) Å, $V = 1624$ (2) Å^3, $Z = 4$, $D_x = 1 \cdot 55$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 729$ mm^{-1}, $F(000) = 792$, $T = 118$ (1) K, ferroelectric structure, $R = 0 \cdot 036$ for 5951 unique reflections. The molecule is deformed slightly from the reported paraelectric structure. Short atomic distances are seen for Ca–O bonds. Major positional differences between the two phases are found in O atoms and CH$_3$ groups, which also exhibit relatively large thermal vibrations.

Introduction. Tris-sarcosine calcium chloride (TSCC), CaCl$_2$.3(CH$_3$NH$_2^+$CH$_2$COO$^-$), undergoes a ferroelectric phase transition at about $T_c = 127$ K (Pepinsky & Makita, 1962). Dielectric and thermal properties (Makita, 1965; López-Echarri & Tello, 1981) suggest that the phase transition is of the order–disorder type. Indeed, dielectric critical slowing down was observed in the GHz region around T_c (Deguchi, Aramaki, Nakamura & Tanaka, 1983). On the other hand, the soft phonon modes were found in the far-IR region by spectroscopic studies (Prokhorova, Smolensky, Siny, Kuzminov, Mikvabia & Arndt, 1980; Chen, Schaack & Winterfeldt, 1981; Kozlov, Volkov, Scott & Feldkamp, 1983). To reconcile this with the controversy about the transition mechanism, Chen & Schaack (1984) proposed a pseudospin–phonon coupled model. In order to clarify the mechanism of the phase transition, it is necessary to determine the crystal structures of TSCC both above and below the phase-transition temperature. The paraelectric structure at room temperature has already been reported (Ashida, Bando & Kakudo, 1972). Hence, we determined the ferroelectric structure at 118 K as part of a continuing study of the mechanism of the phase transition from the structural point of view.
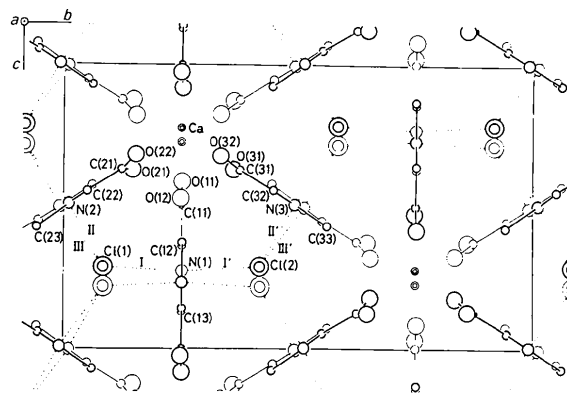
Experimental. Single crystals grown by slow cooling of aqueous solution at about 320 K. Spherical specimen, diameter 0·40 mm. Rigaku AFC-5 diffractometer with graphite monochromator. 25 reflections in range $17 < \theta < 22°$ for measuring lattice parameters. ω–2θ scan mode. 6848 independent reflections measured with $2\theta < 90°$. 6378 observed [$|F_o| > \sigma(|F_o|)$]; 427 of these rejected because of the extinction effect and unbalanced backgrounds. Lorentz–polarization correction. No absorption correction ($\mu r = 0 \cdot 15$). Systematic absences: $hk0$ for h odd, $0kl$ for $k + l$ odd. $Pn2_1a$ because of polar phase. Three standard reflections measured after every 200 reflections, intensity fluctuations within 5% during data collection. Anisotropic full-matrix least-squares

Table 1. *Fractional coordinates and thermal parameters U_{eq} ($\mathrm{\AA}^2 \times 10^2$) with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Ca	0·03820 (2)	0·25	0·22421 (2)	0·710 (3)
Cl(1)	0·48664 (8)	0·08389 (4)	0·71533 (7)	1·41 (1)
Cl(2)	0·49575 (5)	0·41780 (5)	0·71399 (6)	1·39 (1)
Molecule 1				
O(11)	0·1681 (1)	0·2522 (2)	0·4165 (1)	1·91 (2)
O(12)	0·4059 (1)	0·2490 (2)	0·4744 (1)	1·46 (2)
N(1)	0·3514 (1)	0·2519 (2)	0·7299 (1)	1·07 (2)
C(11)	0·2716 (1)	0·2510 (2)	0·4970 (1)	1·06 (2)
C(12)	0·2239 (1)	0·2517 (2)	0·6400 (1)	1·11 (2)
C(13)	0·3054 (2)	0·2522 (2)	0·8694 (1)	1·90 (3)
Molecule 2				
O(21)	0·6656 (2)	0·1475 (1)	0·3746 (2)	1·55 (3)
O(22)	0·9037 (2)	0·1540 (1)	0·3206 (2)	1·92 (4)
N(2)	0·6944 (2)	0·0111 (1)	0·4952 (2)	1·19 (3)
C(21)	0·7954 (2)	0·1244 (1)	0·3739 (2)	1·04 (4)
C(22)	0·8295 (2)	0·0507 (1)	0·4477 (3)	1·09 (4)
C(23)	0·7275 (3)	−0·0567 (2)	0·5763 (3)	2·09 (5)
Molecule 3				
O(31)	0·6468 (2)	0·3613 (1)	0·3718 (2)	1·89 (4)
O(32)	0·8809 (2)	0·3345 (1)	0·3239 (2)	2·37 (4)
N(3)	0·7076 (2)	0·4916 (1)	0·4947 (2)	1·11 (3)
C(31)	0·7819 (2)	0·3744 (1)	0·3740 (2)	1·14 (4)
C(32)	0·8328 (2)	0·4459 (1)	0·4459 (2)	1·11 (3)
C(33)	0·7557 (3)	0·5608 (2)	0·5713 (3)	2·28 (6)

refinement, isotropic for H atoms fixed to the reduced isotropic values of bonded atoms. Paraelectric positional parameters (Ashida *et al.*, 1972) as initial ones; $\sum w(|F_o| - |F_c|)^2$ minimized. Final $R = 0.036$ for $w = 1$. $(\Delta/\sigma)_{max}$ in final refinement cycle 0·26 for non-hydrogen atoms and 2·7 for hydrogen atoms. Residual density in the range $-0.3 < \Delta\rho < 0.5\,e\,\mathrm{\AA}^{-3}$. Scattering factors for neutral atoms and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974). HITAC M-200H computer. *UNICS* program system (Sakurai, 1967).

Discussion. The transition temperature T_c changed from 132 to 128 K by X-ray irradiation during measurement of about 80 h. However, the measurement was made safely in the ferroelectric phase. Atomic parameters are given in Table 1.* The structure is depicted in Fig. 1. The mirror symmetry in the paraelectric phase is lost in the ferroelectric phase. The mirror-symmetrically related Cl⁻ ions and the sarcosine molecules in the paraelectric phase now become independent.

The skeleton of the sarcosine molecules is nearly planar especially for molecule 1. The relatively large atomic displacements from the plane are observed for three kinds of N atoms. The largest displacement is

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39635 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

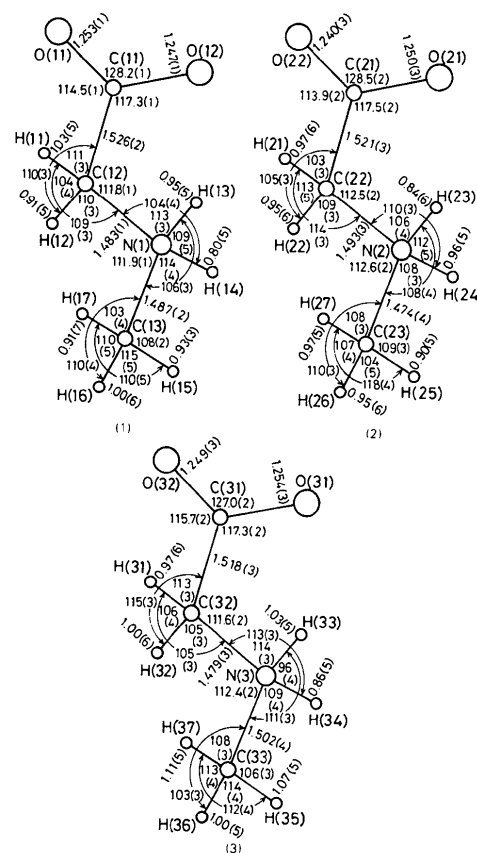0·10 Å for N(2). Bond distances and angles in the molecules are shown in Fig. 2.

The Ca²⁺ ion is surrounded by six O atoms arranged in a slightly deformed octahedron. Atomic distances and angles of the octahedral form are shown in Fig. 3. The Ca—O distances are in the range 2·294 to 2·387 Å, which are shorter than the expected value of 2·40 Å.

Fig. 1. The structure viewed along the *a* axis.

Fig. 2. Bond distances (Å) and angles (°) of the sarcosine molecules.

Table 2. *Hydrogen bonds*

H-bond*	N···Cl (Å)	H···Cl (Å)	∠NHCl (°)	∠C$_a$NCl (°)	∠C^{M}NCl (°)†			
I	3·178(3)	2·27(5)	161(5)	105·9(2)	99·1(2)	N–Cl–N angle (°) between I and II	128·80(5)	
I'	3·178(3)	2·42(6)	160(5)	107·2(2)	99·4(2)	I' and II'	130·20(5)	
II	3·204(2)	2·31(6)	156(5)	122·3(1)	92·4(2)	I and III	106·10(5)	
II'	3·227(2)	2·39(6)	164(5)	118·9(1)	97·6(2)	I' and III'	105·73(5)	
III	3·215(2)	2·24(5)	158(4)	118·0(1)	96·2(1)	II and III	70·05(6)	
III'	3·198(2)	2·39(5)	161(5)	117·7(2)	94·6(2)	II' and III'	69·98(6)	

* Notation as in Fig. 1.
† C^M: the carbon atom of the methyl group.
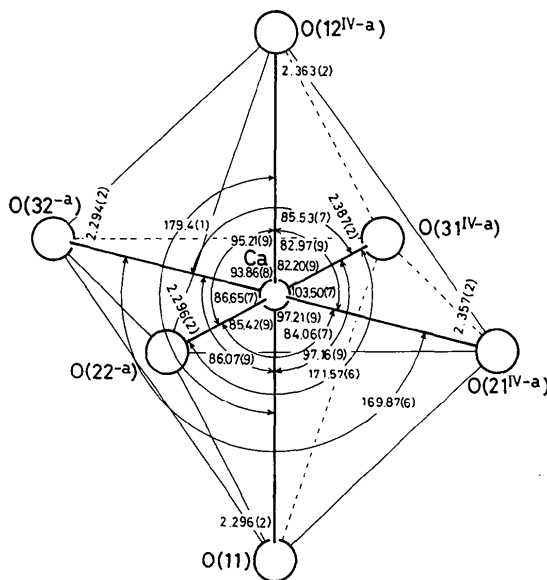
Fig. 3. Atomic distances (Å) and angles (°) of the octahedral arrangement around the Ca^{2+} ion.

Table 3. *Positional differences between the ferroelectric structure* (118 K) *and the paraelectric structure* (*room temperature*)

	aΔx (Å)	bΔy (Å)	cΔz (Å)
Ca	−0·004 (2)	0·0	−0·007 (1)
Cl(1)	−0·042 (2)	0·010 (2)	0·005 (1)
Cl(2)	0·042 (2)	0·019 (2)	−0·008 (1)
Molecule 1			
O(11)	−0·035 (7)	0·039 (3)	0·024 (6)
O(12)	−0·010 (7)	−0·018 (3)	0·026 (5)
N(1)	0·003 (7)	0·032 (3)	0·035 (6)
C(11)	−0·028 (9)	0·017 (3)	0·029 (8)
C(12)	0·010 (8)	0·030 (3)	0·022 (8)
C(13)	0·047 (11)	0·038 (4)	0·036 (9)
Molecule 2			
O(21)	0·062 (5)	0·049 (4)	0·034 (5)
O(22)	0·092 (6)	−0·106 (6)	−0·035 (6)
N(2)	−0·051 (6)	−0·006 (6)	0·015 (6)
C(21)	0·050 (7)	−0·033 (6)	0·007 (6)
C(22)	−0·012 (7)	−0·044 (6)	0·013 (7)
C(23)	−0·096 (9)	0·016 (8)	0·030 (8)
Molecule 3			
O(31)	−0·100 (5)	0·104 (4)	0·005 (5)
O(32)	−0·116 (6)	−0·093 (6)	−0·001 (6)
N(3)	0·069 (6)	0·052 (6)	0·010 (6)
C(31)	−0·073 (7)	0·013 (6)	0·008 (6)
C(32)	0·017 (7)	−0·015 (6)	−0·005 (7)
C(33)	0·162 (9)	0·056 (8)	−0·020 (8)

Such short distances have been reported in the paraelectric phase (Ashida *et al.*, 1972). This fact suggests that thermal motions of atoms in a CaO$_6$ octahedron correlate with each other, leading to the intermolecular correlation of sarcosine molecules along the *a* axis *via* carboxyl radicals.

Dimensions of the hydrogen bond N–H···Cl are listed in Table 2. N···Cl lengths lie in the accepted range (*International Tables for X-ray Crystallography*, 1968). Thermal parameters of the N atoms are smaller than those of the other atoms in the sarcosine molecules. This indicates that N–H···Cl hydrogen bonds play a role in fixing sarcosine molecules with each other *via* Cl⁻ ions. On the other hand, O atoms and CH$_3$ groups, which are located at both ends of the sarcosine molecules, have relatively large thermal amplitudes.

The determined ferroelectric structure was compared with the reported paraelectric one (Ashida *et al.*, 1972). Positional differences between them defined by aΔx = a[x(118 K) − x(RT)] and so on are listed in Table 3. The following characteristic features may be noted. (1) Although positional differences are only within about 0·17 Å, relatively large ones are found in O atoms and CH$_3$ groups. (2) Root-mean-square thermal amplitudes in the paraelectric phase at room temperature are larger than the associated positional differences. This implies that there exists some disordered motion such as a reorientational motion of the CaO$_6$ octahedron in the paraelectric phase. (3) Temperature variation of the mean-square thermal amplitudes is by no means expressed by a straight line passing through the origin in the above temperature range. This result indicates the breakdown of a simple harmonic vibration model.

To clarify the mechanism of the phase transition, structure determinations at several temperatures are now in progress in a wide temperature range above and below T_c.

References

ASHIDA, T., BANDO, S. & KAKUDO, M. (1972). *Acta Cryst.* B28, 1560–1565.
CHEN, T. & SCHAACK, G. (1984). *J. Phys. C*, 17, 3821–3836.
CHEN, T., SCHAACK, G. & WINTERFELDT, V. (1981). *Ferroelectrics*, 39, 1131–1134.
DEGUCHI, K., ARAMAKI, N., NAKAMURA, E. & TANAKA, K. (1983). *J. Phys. Soc. Jpn*, 52, 1897–1900.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KOZLOV, G. V., VOLKOV, A. A., SCOTT, J. F. & FELDKAMP, G. E. (1983). *Phys. Rev. B*, **28**, 255–261.

LÓPEZ-ECHARRI, A. & TELLO, M. J. (1981). *J. Phys. D*, **14**, 71–77.

MAKITA, Y. (1965). *J. Phys. Soc. Jpn*, **20**, 2073–2080.

PEPINSKY, R. & MAKITA, Y. (1962). *Bull. Am. Phys. Soc. Ser.* II, **7**, 241.

PROKHOROVA, S. D., SMOLENSKY, G. A., SINY, I. G., KUZMINOV, E. G., MIKVABIA, V. D. & ARNDT, H. (1980). *Ferroelectrics*, **25**, 629–632.

SAKURAI, T. (1967). Editor. *Universal Crystallographic Computation Program System.* The Crystallographic Society of Japan, Tokyo.

Structure of Tribromotris(pyridine)thallium(III), [TlBr₃(C₅H₅N)₃]

BY S. E. JEFFS, R. W. H. SMALL AND I. J. WORRALL

Department of Chemistry, The University, Lancaster, England

Abstract. $M_r = 681 \cdot 4$, orthorhombic, $P2_12_12_1$, $a = 13 \cdot 39$ (1), $b = 15 \cdot 60$ (2), $c = 8 \cdot 840$ (5) Å, $V = 1846 \cdot 5$ Å³, $Z = 4$, $D_x = 2 \cdot 450$, $D_m = 2 \cdot 56$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7106$ Å, $\mu = 1 \cdot 48$ mm⁻¹, $F(000) = 1248$, room temperature. Final $R = 0 \cdot 050$ for 2064 unique observed reflections. The crystal structure consists of neutral molecules of TlBr₃(C₅H₅N)₃; the configuration around the Tl is a distorted octahedron with *mer* geometry. The *trans* bonds show deviations from linearity within a range of 7–10°; intermolecular effects involving the pyridines are considered to be important in attributing the deviations of the N from regular octahedral sites.

Introduction. The Group III halides InBr₃, InCl₃ and TlCl₃ react with excess pyridine to form complexes of stoichiometry $MX_3 \cdot 4\text{C}_5\text{H}_5\text{N}$ (Small & Worrall, 1982; Jeffs, Small & Worrall, 1984c) which contain $MX_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ molecules with *mer* geometry and an additional pyridine solvate molecule. Under similar conditions TlBr₃ forms only the 3:1 complex. For MX_3 octahedral complexes there are two possible isomers and we have determined the crystal structure of the title compound to see if the other isomer (*fac*) might occur in the absence of the extra solvate molecule.

Experimental. Title compound prepared by adding excess dry pyridine to a solution of Tl^III bromide in acetonitrile. Suitable crystals obtained by recrystallizing from pyridine were transferred to Lindemann tubes in a nitrogen-filled dry box. Crystal data obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1 \cdot 542$ Å); D_m measured by flotation in benzene/methylene dibromide solutions. Intensity measurements made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation; layers $l = 0$–9 measured; $2\theta < 50°$; crystal size $0 \cdot 19 \times 0 \cdot 18 \times 0 \cdot 40$ mm. Absorption corrections (max., min. values 0·06, 0·02) and scaling of data carried out with *SHELX*76 (Sheldrick, 1976). 2461 reflections measured; elimination of those with $I < 3\sigma(I)$ gave 2064 unique reflections. Standards measured every ten reflections: variation 1%. Same programs used for all other calculations. Tl-atom positions, obtained from Patterson maps, used to phase $(F_o - F_c)$ maps to give positions of remaining atoms (apart from H). Full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for Tl and Br, isotropic U values for remaining non-H atoms, convergence at $R = 0 \cdot 050$; $wR = 0 \cdot 056$, $w = 0 \cdot 2962/[\sigma^2(F_o) + 0 \cdot 017182 F_o^2]$. The enantiomorph was also refined and increased R slightly. $(\Delta/\sigma)_{max}$ 0·215; max. in final difference Fourier map $1 \cdot 97$ e Å⁻³ (associated mainly with Tl). No correction applied for secondary extinction. Atomic scattering factors those of Cromer & Mann (1968) and Cromer & Liberman (1970).

Discussion. Final coordinates and equivalent isotropic thermal parameters (U_{eq}) for Tl and Br, and isotropic thermal parameters for C and N are given in Table 1.* The crystal structure contains 'octahedral' neutral molecules TlBr₃·3C₅H₅N with *mer* (*trans*) geometry (Fig. 1) and is similar to that of TlCl₃·3C₅H₅N found in TlCl₃·4C₅H₅N (Jeffs *et al.*, 1984c) but lacks the twofold rotation axis present in that structure. Selected bond distances and angles are listed in Table 2. It is seen that

---

* Lists of structure factors, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39628 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.