Acta Cryst. (1976). B**32**, 1171

The Crystal Structure of the 1:5 Calcium Perchlorate–Diacetamide Complex

By J. P. Roux

Department of Physics, University of the Orange Free State, Bloemfontein 9300, *South Africa*

and G. J. Kruger

Chemical Physics Group, CSIR, P.O. Box 395, *Pretoria* 0001, *South Africa*

(*Received* 16 *September* 1975; *accepted* 19 *September* 1975)

The structure of $Ca(ClO_4)_2.5(C_4H_7NO_2)$ has been determined by X-ray diffraction. Intensities were collected by automatic counting methods and agreement of $R=0{\cdot}079$ was obtained after full-matrix anisotropic refinement. Each Ca ion is chelated by four diacetamide molecules and lies at the centre of an antiprism defined by the eight O ligands. The fifth diacetamide molecule is uncoordinated and in the *cis–trans* planar configuration.

Introduction

The preparation of the complexes of diacetamide ($CH_3CO.NH.COCH_3$, DA) with alkali and alkaline earth metal salts was described by Gentile & Shankoff (1965). The main features of these complexes were explained by the structure determinations of NaBr.2DA, KI.2DA and $CaBr_2.4DA$ (Roux & Boeyens, 1969*a*, *b*, 1970). According to Gentile & Shankoff (1965) the infrared spectra of the complexes $Ca(ClO_4)_2.5DA$ and $Ba(ClO_4)_2.5DA$ indicated monodentation, non-planarity and configuration intermediate between the *trans–trans* and *cis–trans* forms for one of the DA molecules. They concluded that the data were in support of an unusual coordination number of nine. The structure determination of $Ca(ClO_4)_2.5DA$ was undertaken to establish the coordination geometry of this complex and verify the deductions made from the infrared data.

Experimental

The complex was prepared according to the method previously described for $CaBr_2.4DA$ (Roux & Boeyens, 1970). The crystals are monoclinic with $a=20{\cdot}17$ (2), $b=7{\cdot}76$ (1), $c=24{\cdot}38$ (2) Å, $\beta=113{\cdot}7$ (1)°. The systematic absences, $h0l$: $l\neq2n$, indicate space groups $P2/c$ or Pc. The successful structure analysis confirmed $P2/c$. The density was measured as 1·398 and calculated as 1·406 g cm^{-3} for $Z=4$.

Intensities were collected on a Philips PW1100 four-circle diffractometer with a crystal, 0·4 × 0·4 × 0·4 mm, sealed in a Lindemann capillary to prevent decomposition in the atmosphere. Graphite-monochromated Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) was used and intensities collected to a maximum $\sin\theta/\lambda$ of 0·492. An ω-scan mode was used with a scan width of 1° in θ and a scan speed of 0·025° s^{-1}. 3264 reflexions were measured of which 749 were considered to be unobserved with $I<2\sigma$. The intensities of three standard reflexions measured at intervals of 1 h showed that no decomposition of the crystal took place during data collection. No absorption corrections were applied [$\mu(\text{Mo } K\alpha)=3{\cdot}7$ cm^{-1}].

Structure determination and refinement

The structure determination was attempted by direct methods. Acceptable positions for only the Ca and Cl atoms were found from an E map. Two Ca atoms were placed in the special positions $\frac{1}{2},y,\frac{1}{4}$ and $0,y,\frac{1}{4}$ and two Cl atoms in general positions. A Fourier synthesis phased by the contributions of these heavy atoms did not produce meaningful positions for the lighter atoms. A Patterson synthesis revealed the correct positions of the heavy atoms, which differed from the E map solution by a shift in their y coordinates only.

All the non-hydrogen atoms were found from successive Fourier syntheses. Anisotropic refinement by full-matrix least-squares methods converged to a final R of 0·079. No differential weighting was applied. No H atoms were included in the structure factor calculations.

All the calculations were done with the *X-RAY System of Crystallographic Programs* (1972). Scattering factors were those of Cromer & Mann (1968). Final coordinates and thermal parameters are listed in Table 1, interatomic distances and angles in Table 2.*

Structure description

The two independent Ca ions lie on twofold axes and are both chelated to the eight O atoms of four diacetamide molecules. The fifth diacetamide molecule is uncoordinated and contained in a channel along [010],

---

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31393 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and anisotropic temperature factors* ($Å^2 \times 10^3$)

Thermal parameters are in the form $T=\exp [-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	0	−140 (3)	7500	47 (2)	19 (1)	17 (1)	0	8 (1)	0
Ca(2)	5000	5359 (3)	7500	47 (2)	21 (1)	25 (1)	0	2 (1)	0
Cl(1)	1346 (2)	4021 (4)	5258 (1)	74 (2)	65 (2)	54 (2)	−15 (2)	33 (2)	−7 (2)
Cl(2)	3640 (2)	1154 (5)	4775 (1)	77 (2)	104 (3)	53 (2)	−24 (2)	32 (2)	2 (2)
O(1)	845 (6)	2793 (14)	5275 (5)	156 (10)	122 (9)	173 (10)	−61 (8)	94 (9)	−3 (8)
O(2)	1615 (6)	4906 (21)	5796 (5)	145 (10)	301 (18)	151 (10)	−47 (11)	77 (8)	−154 (12)
O(3)	1927 (4)	3286 (12)	5132 (3)	66 (5)	130 (8)	70 (5)	1 (5)	18 (4)	−56 (5)
O(4)	973 (7)	5151 (17)	4794 (6)	192 (12)	171 (12)	223 (14)	74 (10)	118 (11)	131 (12)
O(5)	3165 (9)	2345 (32)	4805 (10)	188 (16)	374 (30)	322 (25)	24 (18)	97 (16)	−174 (24)
O(6)	3746 (10)	149 (25)	5244 (6)	302 (20)	297 (21)	128 (11)	−139 (17)	55 (12)	95 (13)
O(7)	4280 (5)	1803 (17)	4801 (5)	93 (7)	200 (13)	176 (11)	−32 (8)	43 (7)	76 (10)
O(8)	3299 (9)	428 (29)	4235 (5)	257 (17)	421 (28)	95 (9)	−105 (19)	56 (10)	−89 (13)
O(11)	519 (3)	2294 (7)	7226 (3)	76 (5)	31 (4)	36 (4)	−14 (3)	28 (4)	−2 (3)
O(12)	459 (3)	−898 (8)	6742 (3)	83 (5)	30 (4)	40 (4)	1 (3)	37 (4)	4 (3)
N(1)	589 (4)	1667 (9)	6331 (3)	61 (5)	27 (5)	40 (5)	4 (4)	26 (4)	2 (4)
C(11)	574 (5)	2767 (11)	6776 (5)	39 (6)	29 (6)	54 (7)	−2 (4)	19 (5)	3 (5)
C(12)	572 (5)	−109 (12)	6353 (4)	41 (6)	46 (7)	37 (6)	5 (5)	17 (5)	3 (5)
C(13)	629 (7)	4677 (12)	6643 (5)	115 (10)	26 (6)	95 (9)	−11 (6)	55 (8)	12 (6)
C(14)	710 (6)	−1017 (13)	5861 (4)	92 (8)	60 (7)	37 (6)	9 (6)	38 (6)	−5 (5)
O(21)	955 (3)	680 (7)	8452 (3)	62 (4)	28 (4)	27 (3)	2 (3)	−6 (3)	5 (3)
O(22)	793 (3)	−2515 (7)	7945 (2)	61 (4)	32 (3)	25 (3)	12 (3)	8 (3)	0 (3)
N(2)	1444 (4)	−1840 (9)	8928 (3)	62 (5)	32 (5)	29 (4)	8 (4)	5 (4)	2 (4)
C(21)	1306 (5)	−93 (12)	8904 (4)	47 (6)	34 (6)	34 (6)	−6 (5)	7 (5)	−6 (5)
C(22)	1197 (5)	−2955 (11)	8445 (4)	51 (6)	37 (6)	38 (5)	7 (5)	23 (5)	6 (4)
C(23)	1652 (6)	800 (13)	9510 (4)	98 (9)	51 (7)	33 (6)	11 (6)	−7 (6)	−18 (5)
C(24)	1472 (6)	−4788 (11)	8586 (5)	84 (8)	27 (6)	65 (7)	25 (5)	24 (6)	8 (5)
O(31)	4508 (3)	7801 (8)	7818 (3)	62 (4)	34 (4)	53 (5)	12 (3)	19 (4)	7 (4)
O(32)	4560 (4)	4554 (8)	8261 (3)	88 (5)	31 (4)	51 (4)	5 (4)	31 (4)	2 (4)
N(3)	4501 (4)	7089 (10)	8729 (3)	63 (6)	32 (5)	48 (5)	0 (4)	17 (4)	−3 (4)
C(31)	4517 (5)	8325 (13)	8297 (5)	33 (6)	47 (7)	52 (7)	10 (5)	11 (5)	−13 (6)
C(32)	4466 (5)	5300 (13)	8662 (4)	68 (7)	35 (7)	40 (6)	6 (5)	11 (6)	−2 (5)
C(33)	4551 (6)	134 (12)	8474 (5)	87 (8)	28 (6)	96 (9)	−7 (6)	46 (7)	−21 (6)
C(34)	4318 (7)	4373 (13)	9149 (4)	123 (10)	44 (6)	51 (7)	4 (7)	46 (7)	13 (5)
O(41)	4027 (3)	6199 (7)	6565 (3)	63 (4)	32 (4)	42 (4)	−8 (3)	−6 (3)	2 (3)
O(42)	4198 (3)	2999 (7)	7069 (3)	62 (4)	33 (4)	40 (4)	−11 (3)	5 (3)	2 (3)
N(4)	3415 (4)	3772 (10)	6127 (3)	70 (6)	39 (5)	38 (5)	−17 (4)	5 (4)	4 (4)
C(41)	3598 (5)	5456 (12)	6134 (4)	53 (6)	38 (7)	46 (6)	−4 (5)	8 (5)	8 (5)
C(42)	3716 (5)	2617 (11)	6597 (4)	52 (6)	35 (6)	43 (6)	−9 (5)	25 (5)	−6 (5)
C(43)	3191 (7)	6409 (16)	5541 (5)	117 (10)	71 (8)	44 (7)	−22 (8)	−20 (7)	23 (6)
C(44)	3387 (6)	819 (13)	6475 (5)	100 (9)	38 (6)	57 (7)	−39 (6)	21 (6)	−5 (5)
O(51)	2812 (5)	5842 (12)	8098 (5)	120 (8)	65 (6)	139 (9)	−7 (6)	45 (7)	5 (6)
O(52)	2196 (5)	210 (13)	7085 (5)	96 (7)	114 (8)	99 (7)	4 (6)	32 (6)	34 (7)
N(5)	7627 (5)	8636 (12)	7950 (4)	59 (6)	45 (6)	80 (7)	−4 (5)	24 (5)	1 (5)
C(51)	2661 (6)	7005 (18)	7727 (7)	51 (7)	58 (9)	120 (12)	−12 (7)	23 (8)	13 (9)
C(52)	2405 (6)	155 (17)	7631 (7)	40 (7)	82 (10)	95 (10)	−5 (7)	17 (7)	12 (9)
C(53)	2572 (7)	6693 (18)	7086 (6)	114 (11)	112 (11)	69 (9)	−31 (9)	36 (8)	−37 (8)
C(54)	2440 (8)	1697 (17)	8018 (7)	106 (11)	69 (9)	135 (13)	9 (8)	25 (10)	−29 (9)

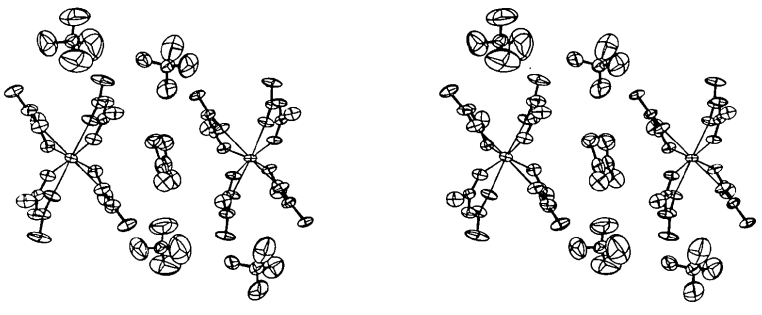

Fig. 1. Stereoscopic view (*ORTEP*-II, Johnson, 1971) down **b** of a part of the unit cell showing the environment of the non-bonded diacetamide molecule. The thermal vibrational ellipsoids are scaled to 50% probability.

formed by the diacetamide edges of two Ca coordination units and two ClO_4 ions. One such channel is illustrated in Fig. 1. This uncoordinated diacetamide molecule is fully rotated into the stable *cis–trans* configuration. It lies halfway between two Ca coordination units with the O atoms tending towards the neighbouring Ca ions with a closest approach of 4·93 Å. The coordination geometry around the Ca ions is antiprismatic with an average Ca–O distance of 2·41 Å. Perspective views of these coordination units are given in Fig. 2 with the interatomic distances and angles indicated.

Table 2. *Bond lengths* (Å) *and angles* (°)

Ca(1)–O(11)	2·382 (9)	Cl(1) –O(1)	1·402 (13)
Ca(1)–O(12)	2·449 (9)	Cl(1) –O(2)	1·383 (14)
Ca(1)–O(21)	2·430 (6)	Cl(1) –O(3)	1·443 (10)
Ca(1)–O(22)	2·394 (8)	Cl(1) –O(4)	1·390 (13)
Ca(2)–O(31)	2·408 (9)	Cl(2) –O(5)	1·353 (24)
Ca(2)–O(32)	2·439 (9)	Cl(2) –O(6)	1·329 (17)
Ca(2)–O(41)	2·423 (6)	Cl(2) –O(7)	1·365 (13)
Ca(2)–O(42)	2·389 (8)	Cl(2) –O(8)	1·340 (14)
N(1)—C(11)	1·390 (14)	N(3)—C(31)	1·390 (15)
N(1)—C(11)	1·380 (13)	N(3)—C(32)	1·396 (14)
C(11)–O(11)	1·204 (14)	C(31)–O(31)	1·207 (15)
C(11)–C(13)	1·531 (15)	C(31)–C(33)	1·530 (15)
C(12)–O(12)	1·223 (13)	C(32)–O(32)	1·215 (14)
C(12)–C(14)	1·512 (16)	C(32)–C(34)	1·516 (17)
N(2)—C(21)	1·380 (13)	N(4)—C(41)	1·356 (13)
N(2)—C(22)	1·383 (11)	N(4)—C(42)	1·388 (12)
C(21)–O(21)	1·204 (10)	C(41)–O(41)	1·206 (10)
C(21)–C(23)	1·523 (13)	C(41)–C(43)	1·534 (14)
C(22)–O(22)	1·211 (9)	C(42)–O(42)	1·206 (9)
C(22)–C(24)	1·516 (14)	C(42)–C(44)	1·522 (14)
		N(5)—C(51)	1·390 (18)
		N(5)—C(52)	1·384 (17)
		C(51)–O(51)	1·226 (18)
		C(51)–C(53)	1·520 (22)
		C(52)–O(52)	1·226 (19)
		C(52)–C(54)	1·508 (21)

O(1)—Cl(1) –O(2)	108·8 (9)	O(5)—Cl(2) –O(6)	103·1 (14)
O(1)—Cl(1) –O(3)	113·2 (7)	O(5)—Cl(2) –O(7)	115·0 (12)
O(1)—Cl(1) –O(4)	107·0 (7)	O(5)—Cl(2) –O(8)	104·2 (12)
O(2)—Cl(1) –O(3)	110·8 (6)	O(6)—Cl(2) –O(7)	110·9 (10)
O(2)—Cl(1) –O(4)	109·6 (9)	O(6)—Cl(2) –O(8)	116·2 (12)
O(3)—Cl(1) –O(4)	107·2 (8)	O(7)—Cl(2) –O(8)	107·6 (10)
C(11)–N(1)—C(12)	125·0 (9)	C(31)–N(3)—C(32)	124·3 (9)
N(1)—C(11)–O(11)	124·3 (8)	N(3)—C(31)–O(31)	124·0 (9)
N(1)—C(11)–C(13)	113·8 (10)	N(3)—C(31)–C(33)	114·4 (10)
O(11)–C(11)–C(13)	121·9 (10)	O(31)–C(31)–C(33)	121·6 (10)
N(1)—C(12)–O(12)	123·0 (9)	N(3)—C(32)–O(32)	123·4 (10)
N(1)—C(12)–C(14)	114·7 (9)	N(3)—C(32)–C(34)	113·4 (10)
O(12)–C(12)–C(14)	122·2 (9)	O(32)–C(32)–C(34)	123·2 (9)
C(21)–N(2)—C(22)	125·6 (7)	C(41)–N(4)—C(42)	125·9 (7)
N(2)—C(21)–O(21)	124·2 (8)	N(4)—C(41)–O(41)	124·5 (8)
N(2)—C(21)–C(23)	113·6 (7)	N(4)—C(41)–C(43)	114·4 (8)
O(21)–C(21)–C(23)	122·2 (9)	O(41)–C(41)–C(43)	121·0 (9)
N(2)—C(22)–O(22)	123·1 (8)	N(4)—C(42)–O(42)	123·0 (8)
N(2)—C(22)–C(24)	114·9 (7)	N(4)—C(42)–C(44)	114·8 (7)
O(22)–C(22)–C(24)	122·0 (8)	O(42)–C(42)–C(44)	122·2 (8)
		C(51)–N(5)—C(52)	127·7 (11)
		N(5)—C(51)–O(51)	114·8 (14)
		N(5)—C(51)–C(53)	122·9 (12)
		O(51)–C(51)–C(53)	122·2 (13)
		N(5)—C(52)–O(52)	122·2 (13)
		N(5)—C(52)–C(54)	113·7 (13)
		O(52)–C(52)–C(54)	124·2 (12)

Figs. 3–5 illustrate the projection of the structure down **b**, **c** and **a**, respectively. The structure is very close to *C*-centred, explaining the systematically weak reflexions with $h+k\neq 2n$. It is the fifth diacetamide molecule with its centre of mass at $\frac{1}{4},y,\frac{1}{4}$ (the position of the screw axis if the lattice were *C*-centred) that lowers the symmetry to $P2/c$.

All the diacetamide molecules, including the uncoordinated one, are very close to planar with a largest deviation from the best plane of 0·129 Å for O(31).

Discussion

This structure determination shows that $Ca(ClO_4)_2.5DA$ is a simple ion–dipole complex in

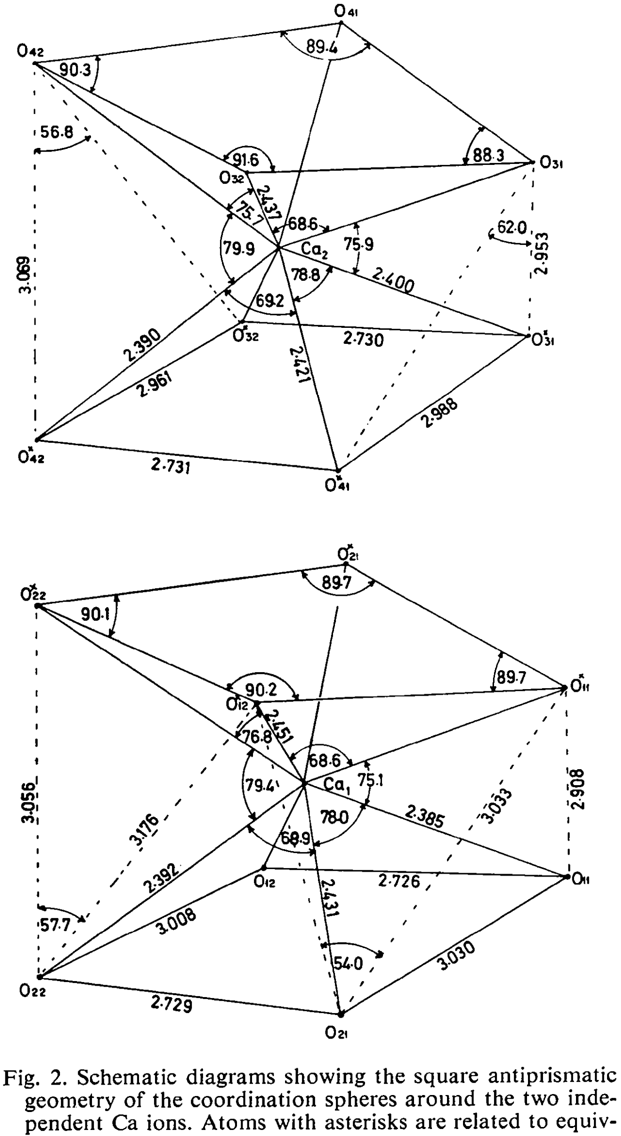

Fig. 2. Schematic diagrams showing the square antiprismatic geometry of the coordination spheres around the two independent Ca ions. Atoms with asterisks are related to equivalent atoms by a twofold axis.

which the Ca atoms have a coordination number of 8. The antiprismatic arrangement of the ligand atoms surrounding the Ca ions is similar to that found in the $CaBr_2.4DA$ complex (Roux & Boeyens, 1970).

The three main deductions made by Gentile & Shankoff (1965) from their infrared data are clearly rejected. (i) There is no possibility of any monodentation of the fifth DA molecule. The closest approach of its carbonyl groups to a neighbouring cation is 4·93 Å. (ii) All the molecules are planar. (iii) The uncoordinated DA molecule is in the fully rotated *trans–cis* configuration and not intermediate between the *trans–trans* and *trans–cis* configurations as predicted.

The *trans–trans* configuration of acetamide is less stable than the *trans–cis* configuration owing to repulsiv forces between the two carbonyl O atoms (Uno & Machida, 1961; Uno, Machida & Hamanaka 1961). One would therefore expect to find the DA molecule not acting as a bidentate ligand to be in the *trans–cis* configuration with its C–O bonds tending to ion–dipole interaction with the neighbouring cations as is the case with the uncoordinated DA molecule in this structure.

The data were collected at the National Physical Research Laboratory of the CSIR in Pretoria. The bulk of the Fourier calculations was done at the computer centre of the University of the Orange Free State, Bloemfontein. The final refinement and the perspective drawings were done at the CSIR computer centre and financed by a CSIR grant. The authors thank Professor E. G. Boonstra for the interest taken in this work and his valuable advice.

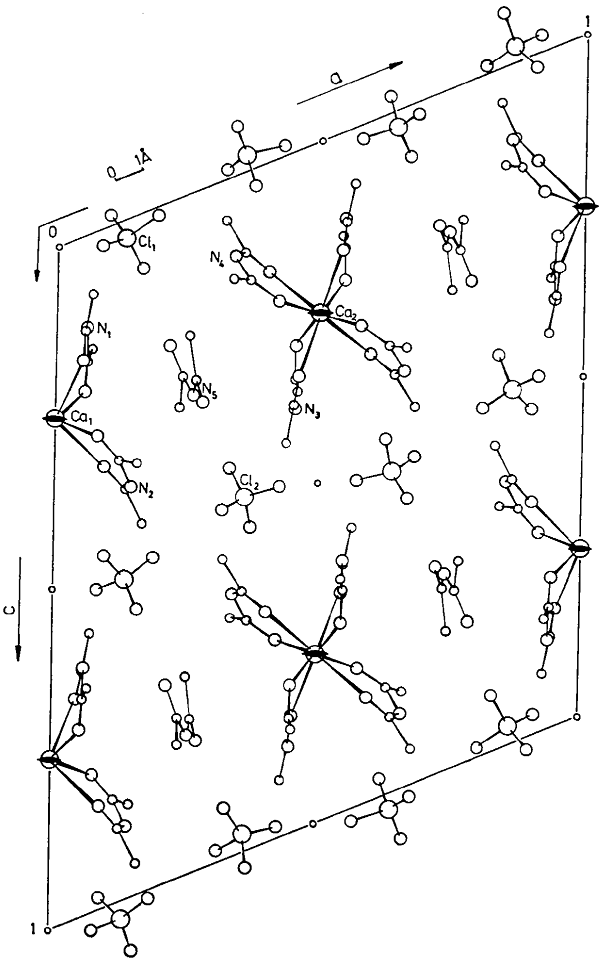

Fig. 3. The contents of the unit cell in projection along [010].

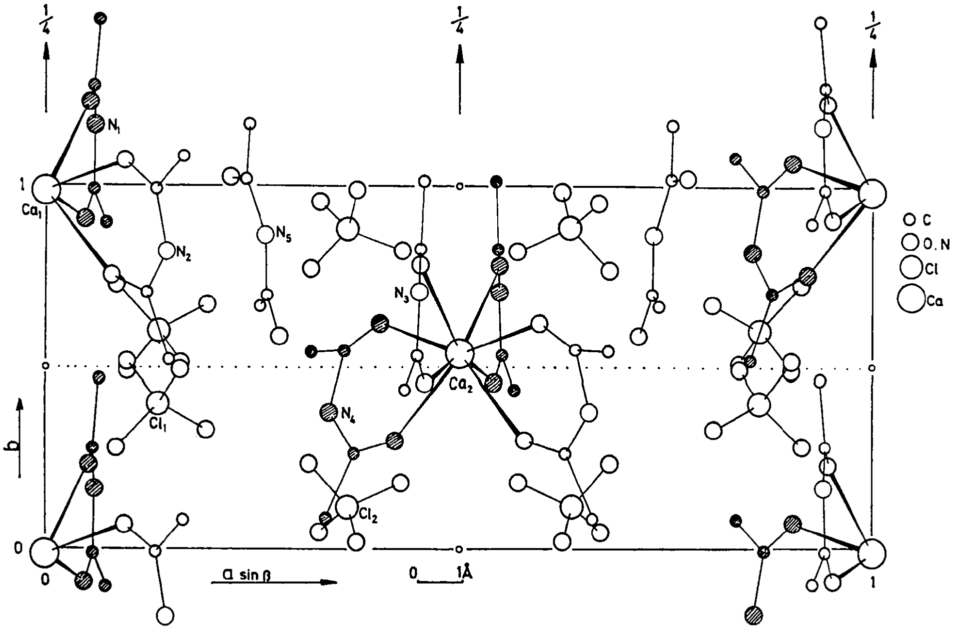

Fig. 4. Projection along [001] showing the coordination units around Ca(1) at $x=0$ and Ca(2) at $x=\frac{1}{2}$ as well as the uncoordinated DA molecule. The units related by the c-glide plane are omitted. The atoms indicated by hatched circles lie below those indicated by open circles in a specific coordination unit.

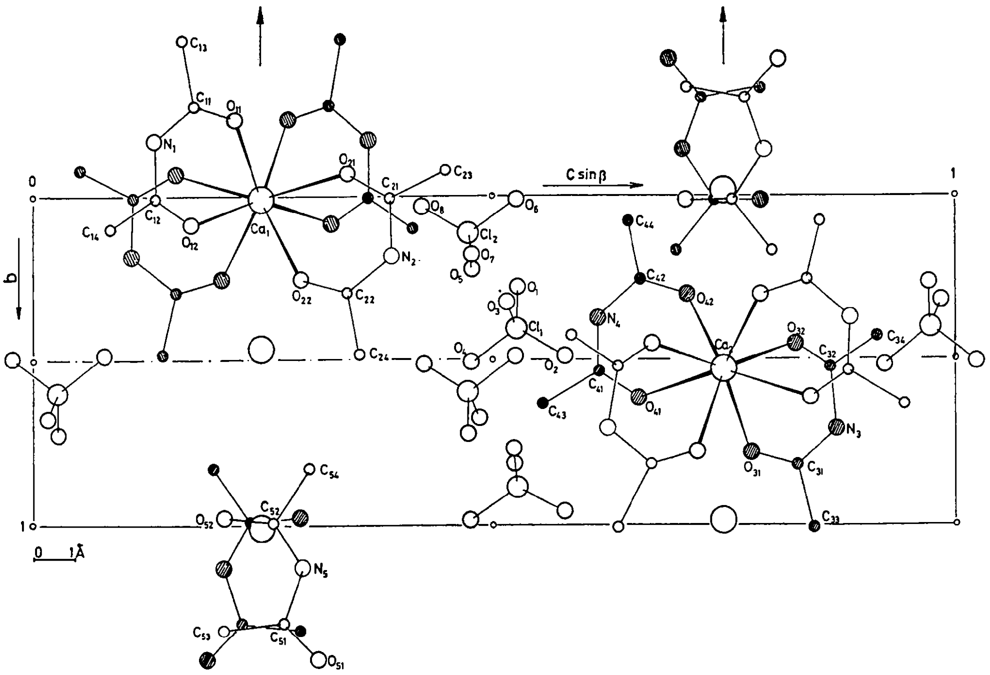

Fig. 5. Projection along [100]. The Ca atoms are at $z=\frac{1}{4}$. The glide-plane related units are omitted. Atoms represented by hatched circles lie below those indicated by open circles.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

GENTILE, P. S. & SHANKOFF, T. A. (1965). *J. Inorg. Nucl. Chem.* **27**, 2301–2309.

JOHNSON, C. K. (1971). *ORTEP*-II. Oak Ridge National Laboratory Report ORNL-3794.

ROUX, J. P. & BOEYENS, J. C. A. (1969*a*). *Acta Cryst.* B**25**, 1700–1703.

ROUX, J. P. & BOEYENS, J. C. A. (1969*b*). *Acta Cryst.* B**25**, 2395–2400.

ROUX, J. P. & BOEYENS, J. C. A. (1970). *Acta Cryst.* B**26**, 526–531.

UNO, T. & MACHIDA, K. (1961). *Bull. Chem. Soc. Japan*, **34**, 545–550.

UNO, T., MACHIDA, K. & HAMANAKA, I. (1961). *Bull. Chem. Soc. Japan*, **34**, 1448–1453.

X-RAY System of Crystallographic Programs (1972). Report TR-192, edited by J. M. STEWART, G. J. KRUGER, H. L. AMMON, C. DICKINSON & S. R. HALL, Computer Science Center, Univ. of Maryland.