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The Crystal and Molecular Structure of Bis(diacetamide)(perchlorato)sodium(I)

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The structure of bis(diacetamide)(perchlorato) sodium(I), $Na[(CH_3CONHCOCH_3)_2ClO_4]$, has been determined from three dimensional X-ray diffraction data using monochromatic CuK_α radiation. The unit cell is monoclinic, space group $P2_1/c$, having dimensions $a = 7.529(3)$ Å, $b = 20.69(2)$ Å, $c = 10.974(5)$ Å, $\beta = 122.4(1)°$, and $Z = 4$. The intensity data were collected on an Enraf–Nonius CAD-4 automated diffractometer. The structure was determined by the heavy atom method and refined anisotropically by block diagonal least squares to a conventional unweighted R factor of 0.078.

The compound is a dimer, each sodium being bonded to six oxygens, one from the perchlorate ion and the other five from the diacetamides, two of which form bridges between the sodium atoms. The dimers form infinite chains along the [001] direction. The units of the chain are held together by hydrogen bonds between an amide group and a perchlorato oxygen. Sodium–oxygen bond distances fall within the range 2.31–2.51 Å. It is believed that this is the first reported structure in which perchlorate is coordinated to a non-transition metal.

Introduction

Bis(diacetamide)(perchlorato)sodium(I) was initially reported by Gentile and Shankoff[1], who prepared the compound by solid–solid interaction as well as from solution. Their infrared studies on the compound show perturbation of the T_d symmetry of the perchlorate group, but this was attributed to hydrogen bonding. Although sodium generally exhibits a coordination number of six, the stoichiometry of the sodium–perchlorato–diacetamide complex, $NaClO_4 \cdot 2DA$, would seem to indicate that the sodium is four-coordinate or that the perchlorate ion is in the coordination sphere. The occurrence of either four-coordinate sodium or coordination of perchlorate is rare, and therefore a single crystal X-ray analysis was undertaken to determine the type of coordination present.

Experimental Section

Preparation

$NaClO_4 \cdot 2DA$ was prepared from solution by the method given in reference 1. Crystals large enough for X-ray work were obtained by dissolving anhydrous sodium perchlorate in methanol, adding the stoichiometric amount of diacetamide, and allowing the solvent to evaporate slowly at room temperature.

X-ray

Since the colorless crystals tend to decompose on prolonged exposure to air, they were mounted inside glass capillaries for all x-ray measurements. Cell parameters were initially determined from an oscillation photograph about the *b*-axis and a Weissenberg photograph of the *h*0*l* zone using nickel-filtered copper radiation. Additional photographs of the *hk*0, 0*kl*, and *h*1*l* zones showed the space group to be $P2_1/c$. Density measurements by flotation indicated there were four molecules per unit cell.

A crystal of approximate dimensions 0.10 mm × 0.15 mm × 0.20 mm was selected for intensity data collection, which was done on an Enraf–Nonius CAD-4 automated diffractometer using a monochromated CuK_α beam. The auto-indexing option was employed, and the cell constants so determined are included in

TABLE I. Crystallographic Data for $Na(diacetamide)_2ClO_4$.

M. W. = 324.5	
Crystallographic System:	Monoclinic
Space Group:	$P2_1/c$
Unit Cell Parameters:	$a = 7.529(3)$ Å[a]
	$b = 20.69(2)$ Å
	$c = 10.974(5)$ Å
	$\beta = 122.4(1)°$
	$V = 1442.5$ Å^3
	$Z = 4$
$d_{calc} = 1.49$ g/cm^3	$\lambda_{CuK\alpha} = 1.5418$
$d_{obs} = 1.54 \pm 0.07$ g/cm^3	$\mu_{CuK\alpha} = 63.3$ cm^{-1}
$F_{000} = 672$	

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.

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Table I. These are in agreement with the parameters obtained from film data. All values were scaled to a single intensity control reflection which was measured after every twentieth reflection. A total of 2729 reflections were collected of which 1330 were considered observed.

Solution and Refinement

The structure was solved by the heavy atom method using computer programs obtained from the National Research Council of Canada[2–8]. A sharpened Patterson map gave the position of the chlorine atom. A three dimensional Fourier map phased on the chlorine atom alone showed the positions of the other non-hydrogen atoms, which when included in the structure factor calculation resulted in a residual of 0.29. Assignment of individual isotropic temperature factors followed by block diagonal least squares refinement of the coordinates, thermal parameters, and scale factor reduced the residual to 0.16. Inclusion and refinement of anisotropic temperature factors dropped the R factor to 0.085.

The proximity of one of the perchlorate oxygens (O_8) to the coordinates $^1/_2$, y, $^1/_4$ indicated that it was probably located on the screw axis. Restricting the atomic coordinates to this special position resulted in lowering the R to 0.078. A difference Fourier map was run and the only hydrogen atom which could not be detected was the one involved in hydrogen bonding. Attempts to refine on the hydrogen positions proved unsuccessful, since C–H bond distances became shorter and isotropic thermal parameters of the hydrogens became larger with successive cycles of refinement.

The mean atomic scattering factors had been corrected for both real and imaginary dispersion effects[9]. The function minimized in the least squares calculations was $R = \Sigma w(|F_o|-k|F_c|)^2$ where the sum is taken over all non-equivalent reflections, w is a weight, and k is a scale factor. A weighting scheme based on counter statistics gave a higher R value, so all observed reflections were given unit weight. Unobserved reflections were not included in the summations. A table of observed and calculated structure factors is available from the Editor. Fractional atomic coordinates and anisotropic thermal parameters are given in Tables II, and III respectively.

TABLE II. Fractional Atomic Coordinates and Isotropic Thermal Parameters.

Atom	*x/a*	*y/b*	*z/c*	*B*
Na	0.6006(6)[a]	0.0297(2)	0.3878(4)	3.3
N_1	0.5027(11)	0.1647(3)	0.5532(7)	3.1
N_2	0.6475(12)	–0.0700(4)	0.1227(9)	4.3
O_1	0.3707(9)	0.0648(3)	0.4618(6)	3.1
O_2	0.7737(10)	0.1083(3)	0.5633(7)	4.0
O_3	0.4388(9)	–0.0523(3)	0.2122(7)	4.0
O_4	0.8075(11)	0.0095(3)	0.2021(8)	4.2
C_1	0.3484(13)	0.1192(4)	0.4936(9)	2.9
C_2	0.1409(15)	0.1406(5)	0.4717(12)	4.1
C_3	0.7107(13)	0.1560(4)	0.5897(9)	3.2
C_4	0.8505(16)	0.2136(5)	0.6684(12)	4.7
C_5	0.4768(15)	–0.0834(4)	0.1344(9)	3.2
C_6	0.3496(17)	–0.1399(5)	0.0430(12)	5.2
C_7	0.8009(14)	–0.228(4)	0.1988(9)	3.3
C_8	0.9593(15)	–0.0146(6)	0.1540(10)	3.4
Cl	0.3470(4)	0.1736(1)	0.1626(2)	3.3
O_5	0.4356(17)	0.1122(4)	0.1899(10)	7.5
O_6	0.2844(18)	0.1915(4)	0.0193(8)	7.5
O_7	0.1903(17)	0.1774(6)	0.1889(13)	11.0
O_8	0.500	0.2180(5)	0.250	12.6
H_{11}	0.48	0.212	0.59	
H_{21}	0.14	0.109	0.50	
H_{22}	0.07	0.175	0.38	
H_{23}	0.16	0.197	0.52	
H_{41}	0.77	0.250	0.70	
H_{42}	0.89	0.220	0.61	
H_{43}	0.97	0.194	0.75	
H_{61}	0.28	–0.128	–0.07	
H_{62}	0.17	–0.123	0.00	
H_{63}	0.26	–0.160	0.08	
H_{81}	1.04	–0.085	0.24	
H_{82}	0.96	0.033	0.13	
H_{83}	0.89	–0.013	0.07	

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.

Results and Discussion

The sodium atom in bis(diacetamide)(perchlorato) sodium(I) exhibits its usual coordination number of six, having geometry intermediate between an octahedron and a trigonal prism. This arrangement of atoms has been observed earlier in NaI · 3DMF (DMF = dimethylformamide)[10]. Of the six oxygens making up the coordination sphere in $NaClO_4 \cdot 2DA$, one (O_5) is from the perchlorate ion and the other five (O_1, O_1', O_2, O_3, O_4) are from diacetamides (Figure 1). Since the compound is actually a dimer, two diacetamide oxygens (O_1, O_1') from bridges between sodium atoms, thus joining the two monomeric units, each of which may be represented emprirically by $NaClO_4 \cdot 2DA$. These two monomeric units are crystallographically equivalent, being related by a center of symmetry. If the geometry about the sodium is considered to be a distorted trigonal prism (D_3 symmetry), then the dimer consists of two of these prisms having one edge in common (Figure 2). The triangular faces perpendicular to the C_3 axes in each

TABLE III. Anisotropic Thermal Parameters as Mean Square Amplitude.[a]

Atom	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{23} \times 10^4$	$U_{13} \times 10^4$	$U_{12} \times 10^4$
Na	362(12)[b]	19(1)	146(5)	–27(3)	351(14)	–24(5)
N_1	214(20)	17(2)	126(10)	–14(7)	200(24)	–15(10)
N_2	298(26)	32(2)	158(13)	–57(9)	296(32)	–41(13)
O_1	280(20)	18(2)	135(9)	–17(6)	276(23)	–9(8)
O_2	265(20)	21(2)	165(10)	–15(7)	270(24)	21(9)
O_3	259(20)	28(2)	144(10)	–31(7)	256(24)	–41(9)
O_4	350(23)	30(2)	198(11)	–77(8)	394(28)	–71(11)
C_1	203(25)	22(2)	104(11)	4(8)	207(29)	6(12)
C_2	271(33)	28(3)	222(19)	1(12)	331(42)	29(16)
C_3	213(25)	19(2)	99(11)	14(8)	159(28)	6(12)
C_4	259(30)	26(3)	176(16)	–42(12)	121(37)	–75(16)
C_5	302(31)	23(3)	105(12)	–21(9)	216(34)	–39(14)
C_6	355(38)	38(4)	199(19)	–80(13)	290(45)	–96(19)
C_7	227(26)	24(3)	103(12)	5(9)	162(30)	10(13)
C_8	246(30)	55(4)	120(14)	4(12)	245(35)	16(18)
Cl	369(7)	19(1)	106(3)	8(2)	265(8)	25(4)
O_5	1009(53)	33(3)	279(17)	96(11)	769(55)	185(19)
O_6	1085(52)	56(3)	126(11)	96(10)	552(42)	273(23)
O_7	606(43)	96(6)	415(25)	104(20)	767(58)	178(26)
O_8	1168(71)	71(5)	293(20)	–126(17)	533(64)	–389(32)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. [b] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.

prism are rotated with respect to each other by an approximate average value of 50° (Figure 3), and the dihedral angle between them is 2.65°.

The two bridged sodium atoms are separated by a distance of 3.724 Å. This is somewhat longer than the corresponding distances in the similar complexes $NaI \cdot 3DMF$ (3.27 Å) and $NaBr \cdot 2CH_3CONH_2$ (3.245 Å) reported by Piret and coworkers[10,11]. This difference may be due to the types of ligands used: diacetamide is bidentate while dimethylformamide and acetamide are monodentate.

The ligands are in the *trans–trans* configuration and the slight distortion that exists is manifested as a fold along the Na–N axes. The dihedral angle between planes O_2–C_3–N_1 and O_1–C_1–N_1 is 4.69°, and the dihedral angle between planes O_4–C_7–N_2 and O_3–C_5–N_2 (Figure 4) is 6.90°. The bite of the ligands (2.74, 2.76 Å) falls within the ranges found[12,13] in the compounds $Ba(ClO_4)_2 \cdot 5DA$ (2.76 Å) and $Sr(ClO_4)_2 \cdot 4DA \cdot H_2O$ (2.73–2.82 Å). The bond distances within the ligand are comparable to those for crystalline acetamide[14].

Probably the most important feature of this structure is the coordination of the perchlorate ion. Although several complexes have been reported in which the perchlorate ion behaves as a weak ligand, its coordination was generally inferred from spectroscopic data[15–20]. In almost all these complexes, the central atom was a transition metal. At least three compounds have been reported in which perchlorate coordination was proven by X-ray crystallography, but these structures contained cobalt[21,22] and copper[23] as the central metals.

The Na–O distances involving the perchlorato oxygen (2.51 Å) and the bridging oxygens (2.49 Å) are significantly larger than those involving the other diacetamide oxygens (2.31–2.39 Å). The perchlorato bond distance, as is characteristic of the transition metal complexes, indicates the relatively weak coordinating ability of the perchlorate ion. The isotropic thermal parameter of the coordinated perchlorato oxygen is low, as would be expected for a rigidly held atom.

The complex is bonded intermolecularly via hydrogen bonds between a perchlorato oxygen (O_6) and an amide group (N_2). The effect is to form infinite chains parallel to [001]. The bond distance between the Cl atom and O_6 is significantly larger than the other Cl–O distances. Distortion of the tetrahedral symmetry of the perchlorate is due almost entirely to hydrogen bonding, while coordination produces very little, if any, distortion[24]. It is for this reason that hydrogen bonding, but not coordination, can be detected in the infrared spectrum[1].

All pertinent interatomic distances and angles are found in Tables IV and V and in Figures 4 and 5. The packing diagram is given in Figure 6.

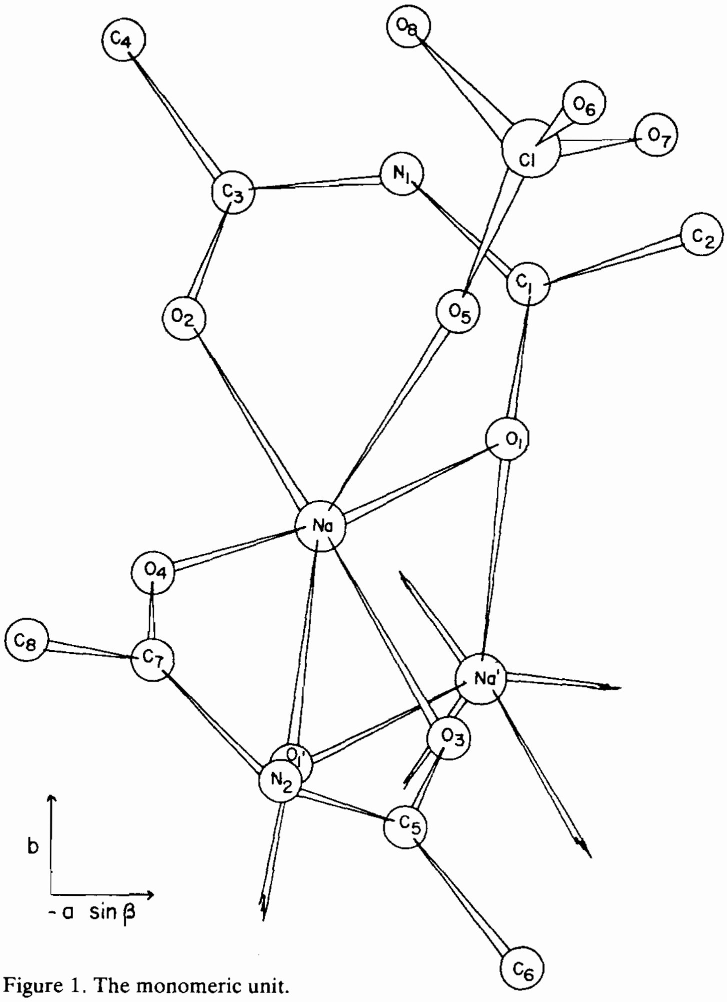

Figure 1. The monomeric unit.

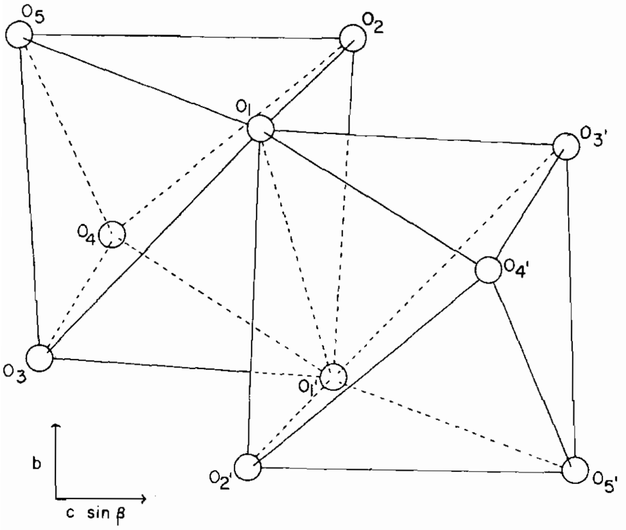

Figure 2. Coordination sphere for the dimeric unit.

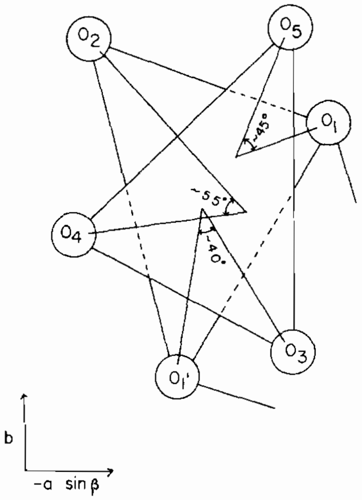

Figure 3. Coordination sphere of the monomer showing projection angles of rotation between opposite triangular faces.

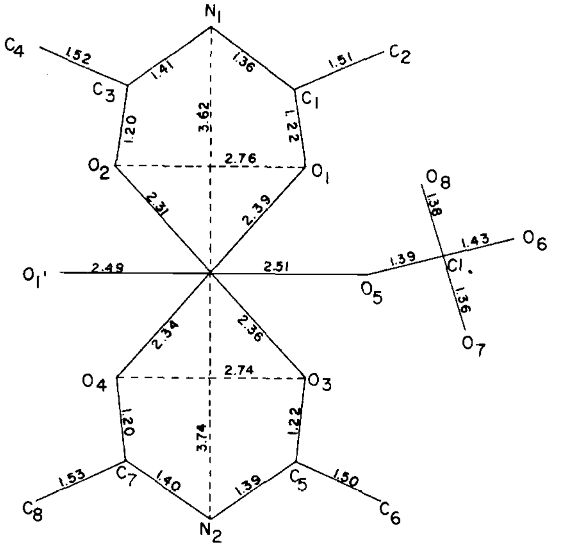

Figure 4. Interatomic distances.

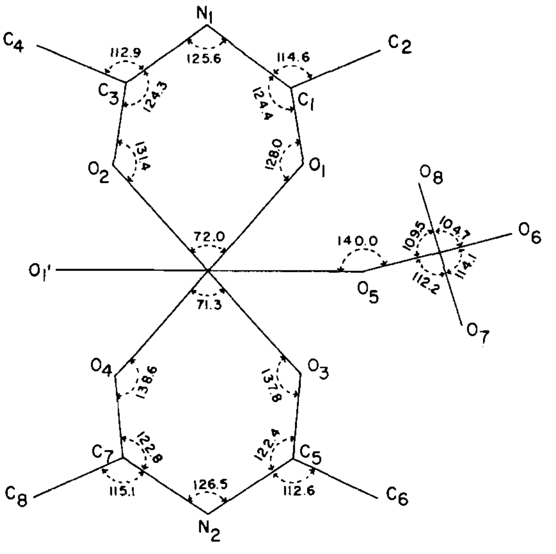

Figure 5. Bond angles.

TABLE IV. Interatomic Distances (Å).

Bond distances in coordination sphere			
Na–O$_1$	2.385(9)[a]	Na–O$_4$	2.337(10)
Na–O$_2$	2.314(7)	Na–O$_5$	2.505(9)
Na–O$_3$	2.358(7)	Na–O$_1'$	2.492(7)
Distances within ligands			
N$_1$–C$_1$	1.36(1)	N$_2$–C$_5$	1.39(2)
N$_1$–C$_3$	1.41(1)	N$_2$–C$_7$	1.40(1)
C$_1$–O$_1$	1.22(1)	C$_5$–O$_3$	1.22(1)
C$_3$–O$_2$	1.20(1)	C$_7$–O$_4$	1.20(1)
C$_1$–C$_2$	1.51(2)	C$_5$–C$_6$	1.50(1)
C$_3$–C$_4$	1.52(1)	C$_7$–C$_8$	1.53(2)
Distances within perchlorato group			
Cl–O$_5$	1.392(9)	Cl–O$_7$	1.359(15)
Cl–O$_6$	1.427(9)	Cl–O$_8$	1.380(7)
Pertinent non-bonded distances			
Na–Na'	3.724(6)	O$_1$–O$_2$	2.76(1)
Na–N$_1$	3.615(8)	O$_3$–O$_4$	2.74(1)
Na–N$_2$	3.735(10)		
Hydrogen bonded distance			
N$_2$–O$_6$	3.14(1)		
Bond distances involving hydrogen atoms			
N$_1$–H$_{11}$	1.1		
C$_2$–H$_{21}$	0.7	C$_4$–H$_{41}$	1.1
C$_2$–H$_{22}$	1.1	C$_4$–H$_{42}$	0.8
C$_2$–H$_{23}$	1.2	C$_4$–H$_{43}$	0.9
C$_6$–H$_{61}$	1.1	C$_8$–H$_{81}$	1.6
C$_6$–H$_{62}$	1.2	C$_8$–H$_{82}$	1.0
C$_6$–H$_{63}$	1.0	C$_8$–H$_{83}$	0.8

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number. [b] Primes refer to atoms at the equivalent positions $-x, -y, -z$ relative to the asymmetric unit x, y, z.

TABLE V. Bond Angles (°).

Angles involving perchlorato group			
O$_5$–Cl–O$_6$	108.0(6)[a]	O$_6$–Cl–O$_7$	114.1(7)
O$_5$–Cl–O$_7$	112.2(7)	O$_6$–Cl–O$_8$	104.7(5)
O$_5$–Cl–O$_8$	109.5(5)	O$_7$–Cl–O$_8$	108.1(6)
Angles involving sodium			
O$_1$–Na–O$_2$	72.0(3)	O$_1$–Na–O$_3$	110.2(3)
O$_3$–Na–O$_4$	71.3(3)	O$_2$–Na–O$_4$	106.7(3)
O$_5$–Na–O$_1$	88.6(3)	O$_1'$–Na–O$_1$	80.4(2)
O$_5$–Na–O$_2$	92.3(3)	O$_1'$–Na–O$_2$	100.9(3)
O$_5$–Na–O$_3$	89.0(3)	O$_1'$–Na–O$_3$	78.5(3)
O$_5$–Na–O$_4$	82.7(3)	O$_1'$–Na–O$_4$	108.4(3)
Na–O$_5$–Cl	140.0(7)	O$_1'$–Na–O$_5$	159.2(3)
Na–O$_1$–C$_1$	128.0(6)	Na–O$_3$–C$_5$	137.8(7)
Na–O$_2$–C$_3$	131.4(6)	Na–O$_4$–C$_7$	138.6(7)
Na–O$_1$–Na'	99.6(3)		
Angles within ligand			
O$_1$–N$_1$–C$_1$	124.4(8)	O$_3$–C$_5$–N$_2$	122.4(9)
O$_1$–C$_1$–C$_2$	120.9(9)	O$_3$–C$_5$–C$_6$	125.0(10)
N$_1$–C$_1$–C$_2$	114.6(8)	N$_2$–C$_5$–C$_6$	112.6(9)
C$_1$–N$_1$–C$_3$	125.6(8)	C$_5$–N$_2$–C$_7$	126.5(8)
O$_2$–C$_3$–N$_1$	124.3(9)	O$_4$–C$_7$–N$_2$	122.8(9)
N$_1$–C$_3$–C$_4$	112.9(8)	N$_2$–C$_7$–C$_8$	115.1(9)
Dihedral angles			
O$_1$–O$_2$–O$_1'$ and O$_3$–O$_4$–O$_5$	2.65		
O$_2$–C$_3$–N$_1$ and O$_1$–C$_1$–N$_1$	4.69		
O$_4$–C$_7$–N$_2$ and O$_3$–C$_5$–N$_2$	6.90		
C$_1$–N$_1$–C$_3$ and O$_1$–O$_2$–C$_3$–C$_1$	2.78		
C$_5$–N$_2$–C$_7$ and O$_3$–O$_4$–C$_5$–C$_7$	1.77		

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.

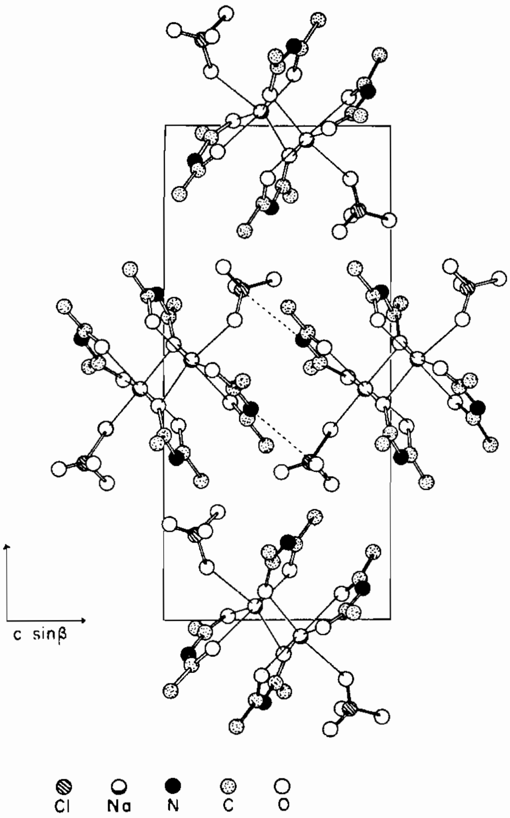

Figure 6. Packing diagram showing contents of unit cell.

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