case of an extremely high-quality crystal and a centro-symmetric structure with a small number of parameters. The accuracy of this structure is characteristic of the best attainable by present-day neutron diffraction techniques.

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Metal Binding to Nucleic Acid Constituents. The Crystal Structure of Trichloroadeniniumzinc(II)

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The crystal structure of a zinc(II) complex of adenine, crystallized from hydrochloric acid solution, has been determined. The compound, trichloroadeniniumzinc(II), $C_5H_6N_5Cl_3Zn$, crystallizes in the space group $P2_1/c$ with unit-cell parameters $a = 10\cdot847(2)$, $b = 5\cdot934(1)$, $c = 15\cdot726(2)$ Å, $\beta = 90\cdot95(2)$, $Z = 4$. Three-dimensional data were collected from two crystals using a Supper two-circle diffractometer. The structure was refined by full-matrix least-squares calculations, minimizing $\sum w(F_o - sF_c)^2$, to a final R of $0\cdot035$. The zinc atom is coordinated to the three chlorine atoms and to N(7) of the adenine moiety in a distorted tetrahedral arrangement.This indicates that N(7) is a possible coordination site for bivalent metal ion interaction with nucleic acids. The six-membered ring of the adenine moiety, which is protonated at N(1), is significantly non-planar. There is an extensive network of intra- and intermolecular hydrogen bonds.

Introduction

The importance of bivalent metal ions in biochemical processes is well known, and their interactions with the bases of nucleotides and nucleic acids have been the subject of numerous studies (*e.g.* Weser, 1968; Eichhorn, Berger, Butzow, Clark, Rifkin, Shin & Tarien, 1971, and references therein). Shin & Eichhorn (1968) have shown that zinc(II) ions can be used to unwind and rewind double-helical DNA reversibly by heating and cooling respectively. It has also been shown that zinc(II)

and other transition metal ions affect the single-helix ⇌ random-coil equilibrium in polyriboadenylic acid (Shin, Heim & Eichhorn, 1972). In many of these, and other similar phenomena, binding of the transition metal ions to the bases has been postulated.

As an aid in the interpretation of these results it is important to establish which sites on the bases are the primary coordination sites for bivalent metals under a variety of conditions, and to obtain a quantitative measure of the electronic changes that occur within the bases as a consequence of metal-binding. Accord-

ingly, a program of crystal structure analyses of metal–nucleic acid base complexes has been commenced in this laboratory.

Several such crystal structure analyses have already been reported; these have recently been summarized by Sundaralingam & Carrabine (1971). The structure described here is that of a complex between zinc(II) and adenine crystallized from acid solution in which the transition metal is coordinated at N(7), a site on the base that is available for coordination in a biological system. A preliminary account of this work has been published (Srinivasan & Taylor, 1970).

Experimental

Crystal data

Following the method of Weitzel & Spehr (1958), good crystals were obtained by slow evaporation of 2:1 mixtures of zinc chloride and adenine in acid solution. The crystals were hard, acicular, colourless
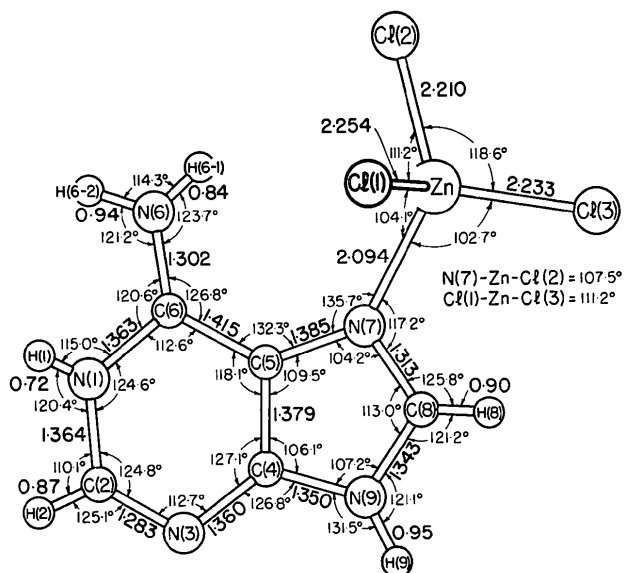

Fig. 1. Interatomic distances and angles in the trichloro-adeniniumzinc(II) molecule. Standard deviations in interatomic distances are: Zn–Cl, 0·002; Zn–N, 0·005; C–C(N), 0·008; H–C(N), 0·07 Å; and 0·3° in angles.
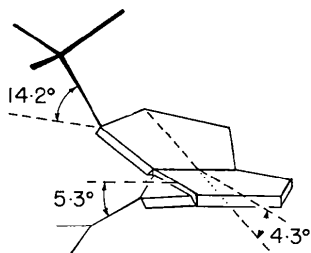

Fig. 2. A schematic representation of the relationship between planar segments of the molecule.

prisms elongated along **b** with the {100} and {001} faces developed.

The space group was determined from an examination of systematic absences on precession photographs. Unit-cell parameters were obtained from the 2θ values of several high-angle reflexions on the zero levels of the diffraction patterns of two different crystals, measured on a two-circle diffractometer. The density was measured by flotation in mixtures of acetone and dibromomethane. Crystallographic data are given in Table 1.

Table 1. *Crystal data*

Trichloroadeniniumzinc(II)	$C_5H_6N_5Cl_3Zn$
Monoclinic	Space group: $P2_1/c$
$a = 10\cdot847$ (2) Å	$F(000) = 608$
$b = 5\cdot934$ (1)	F.W. 307·87
$c = 15\cdot726$ (2)	$V = 1012\cdot08$ Å^3
$\beta = 90\cdot95$ (2)°	$Z = 4$
$D_x = 2\cdot020$ g cm^{-3}	μ(Cu $K\alpha$) = 104·8 cm^{-1}
$D_m = 2\cdot03$ (1)	λ(Cu $K\alpha$) = 1·5418 Å

Intensity measurements

The intensity data were recorded on a Supper automatic two-circle equi-inclination diffractometer using nickel-filtered Cu $K\alpha$ radiation. For each reflexion, the optimum scan speed (to make the ratio $\sigma(I)/I$ for all reflexions approximately the same) was estimated from an initial fast scan. The maximum and minimum scan ranges were 2 and 4° and the scan speeds ranged from 0·05 to 0·33° sec^{-1}. Further details of the diffractometer and its mode of operation are given by Freeman, Guss, Nockolds, Page & Webster (1970).

One crystal, with dimensions 0·275 by 0·213 by 0·103 mm along **a***, **b***, and **c*** respectively, was used to collect data from layers $h = 0$–8, and another, with dimensions 0·25 by 0·313 by 0·128 mm along **a***, **b***, and **c*** respectively, to collect layers $k = 0$–5. Absorption corrections were calculated and applied (Busing & Levy, 1957). The data were scaled by the method of Rae (1965) to give a set of 1831 independent reflexions, of which 195 had an intensity that was less than 2·5 standard deviations above background. These were classified as unobserved, and were given a theoretical value and standard deviation according to Hamilton (1955). Standard deviations for observed reflexions were calculated from a combination of counting statistics and mean deviations for those intensities measured more than once (68 % of the data), and counting statistics alone for the remainder.

Structure determination and refinement

Computational procedures

The following computer programs were used in this analysis: diffractometer control, Freeman *et al.* (1970); data reduction, J. F. Blount, University of Sydney; *PREPFLS* and *FOURIER*, modifications of the data packing and Fourier programs of F. R. Ahmed,

Division of Pure Physics, N. R. C. Ottawa, by M. R. Snow, The University of Adelaide; *FUORFLS*, modification of Busing & Levy's *ORFLS* by M. R. T. for the CDC 6400 computer at the University of Adelaide; and *ORTEP*, C. K. Johnson (1965).

The atomic scattering factors for Zn^{2+}, Cl^-, N, and C were taken from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). The real part of the anomalous dispersion correction was applied for Zn^{2+} ($\Delta f' = -1\cdot7$) and Cl^- ($\Delta f' = +0\cdot3$) as listed in *International Tables for X-ray Crystallography* (1962).

The function minimized in full-matrix least-squares refinement was $\sum w(\Delta F)^2$, where $w = 1/\sigma^2(|F_o|)$. The assignment of standard deviations is described earlier.

Unobserved reflexions were not included in the refinement.

Solution and refinement

The zinc and chlorine atom coordinates were determined from a Patterson function, and the remaining non-hydrogen atoms from a Fourier synthesis. This model was refined by full-matrix least-squares calculations, with individual isotropic temperature factors for all atoms to an R index of $0\cdot096$, followed by one cycle with anisotropic temperature factors to give an R index of $0\cdot066$. At this stage the hydrogen atoms were located in a difference map and included in the calculations with isotropic temperature factors. Attempts to refine the hydrogen-atom parameters resulted in negative temperature factors for some of these atoms. An inspection of the data showed that the observed structure factors for many of the intense reflexions were very much less than their calculated values. In the expectation that this effect was caused by extinction, a secondary extinction parameter was included in the refinement (Larson, 1967). After refining the extinction parameter, scale factor, and non-hydrogen atomic parameters in one cycle the hydrogen atom parameters were refined alone, and now gave physically

reasonable results. Two further cycles, which included all atomic parameters, the extinction parameter, and scale factor (152 parameters), were sufficient to cause the refinement to converge, with the final shifts all being less than one-quarter of their standard deviations. Data for three strong reflexions, 110, 200, and 702, which made abnormally high contributions to $\sum w(\Delta F)^2$, were omitted from these final cycles. No satisfactory explanation can be offered for the large discrepancies between $|F_o|$ and $|F_c|$ for these reflexions.

The R index for the data used in the final refinement cycle was $0\cdot035$ and for the complete data set, including unobserved reflexions, was $0\cdot044$. The final value of the goodness-of-fit was $2\cdot6$. The value of g, the secondary extinction parameter, was 4×10^{-6}. The final atomic parameters and their standard deviations, estimated from the inverted full matrix, are listed in Table 2(a) and (b). Table 3 is a listing of observed structure factors, their standard deviations used in the refinement, and calculated structure factors.

Description and discussion

Zinc coordination

The compound exists in the crystal as discrete trichloroadeniniumzinc(II) molecules in which the zinc atom is tetrahedrally coordinated to the three chlorine atoms and to N(7) of the adenine moiety, which is protonated at N(1). Interatomic distances and angles in the molecule are shown in Fig. 1. Standard deviations, estimated from the inverted full matrix are Zn-Cl, $0\cdot002$; Zn-N, $0\cdot005$; C-C (or N), $0\cdot008$; and H-C (or N), $0\cdot07$ Å in interatomic distances, and $0\cdot3°$ in angles other than hydrogen.

The ligand atoms are not symmetrically situated around zinc; the three chlorine–zinc–chlorine angles range from $111\cdot2$ to $118\cdot6°$, and the zinc–chlorine bond lengths are significantly different from each other. These differences reflect the different environments of the chlorine atoms in the structure. The zinc tetra-

Table 2. *The final atomic parameters*

(a) Non-hydrogen atoms

All values are $\times 10^4$. Standard deviations are in parentheses.

Temperature factor $= \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	2143 (1)	7606 (1)	6546 (1)	43 (1)	144 (3)	19 (1)	9 (1)	−5 (1)	−5 (1)
Cl(1)	773 (1)	5341 (3)	7187 (1)	51 (1)	203 (6)	26 (1)	−11 (2)	−5 (1)	13 (1)
Cl(2)	1203 (1)	10127 (3)	5729 (1)	68 (2)	172 (6)	29 (1)	35 (3)	−3 (1)	8 (2)
Cl(3)	3600 (1)	8778 (3)	7463 (1)	61 (2)	282 (7)	34 (1)	−6 (3)	−17 (1)	−33 (2)
N(1)	1946 (5)	2908 (10)	3767 (3)	46 (5)	183 (20)	20 (2)	13 (8)	−11 (2)	−8 (5)
C(2)	2805 (6)	1232 (12)	3738 (4)	80 (9)	181 (24)	21 (2)	12 (11)	−2 (3)	−17 (6)
N(3)	3684 (5)	959 (9)	4283 (3)	61 (5)	181 (19)	24 (2)	27 (8)	−3 (2)	−23 (5)
C(4)	3673 (5)	2527 (10)	4914 (3)	44 (5)	153 (21)	20 (2)	5 (9)	2 (3)	−2 (6)
C(5)	2863 (5)	4301 (10)	4996 (3)	30 (5)	125 (20)	21 (2)	7 (8)	−1 (2)	−1 (5)
C(6)	1928 (5)	4569 (11)	4366 (3)	34 (5)	156 (21)	17 (2)	−5 (8)	−3 (2)	0 (5)
N(6)	1104 (5)	6164 (11)	4326 (3)	57 (5)	214 (22)	27 (2)	42 (9)	−15 (3)	−18 (6)
N(7)	3116 (4)	5436 (9)	5749 (3)	36 (4)	170 (18)	21 (2)	19 (7)	−6 (2)	−10 (5)
C(8)	4051 (5)	4335 (12)	6087 (4)	41 (5)	219 (24)	20 (2)	18 (9)	−9 (3)	−16 (6)
N(9)	4425 (4)	2603 (9)	5606 (3)	43 (4)	190 (20)	26 (2)	42 (8)	−9 (2)	−14 (5)

Table 2 (cont.)

(b) Hydrogen atoms

Positional parameters are × 10³.
Temperature factor = exp ($- B \sin^2 \theta/\lambda^2$).
Standard deviations are in parentheses.

	x	y	z	B
H(1)	147 (6)	299 (12)	345 (4)	2·9 (1·6)
H(2)	268 (7)	41 (12)	329 (4)	4·9 (1·9)
H(6–1)	108 (6)	724 (10)	467 (4)	2·5 (1·5)
H(6–2)	58 (6)	632 (12)	385 (4)	3·2 (1·5)
H(8)	444 (5)	467 (10)	658 (4)	2·4 (1·3)
H(9)	506 (6)	162 (12)	580 (4)	3·6 (1·7)

hedron is oriented so that Cl(2) and Cl(3) are close to the plane of the adenine moiety, and the Zn–Cl(1) bond is approximately normal to it. The Zn–N(7) bond makes an angle of 14·2° to the plane of the imidazole ring (Fig. 2)

Interatomic distances in the adeninium ligand

The bond lengths and angles within the adenine ring system are in agreement with those in other protonated adenine systems, such as in 3′-adenosine monophosphate dihydrate (Sundaralingam, 1966). The C(8)–N(9) and N(9)–C(4) distances are slightly shorter in this structure than in 3′-AMP, but this can be ascribed to the presence of the N(9) substituent in the

latter compound. Zinc coordination at N(7) to the imidazole ring does not appear to perturb the interatomic distances and angles in the adenine ligand appreciably.

The C(6)–N(6) distance of 1·302 Å indicates that the amino nitrogen lone-pair is strongly delocalized.

Planarity of the adeninium ligand

The results of least-squares planes calculations through selected atoms of the adenine moiety are given in Table 4. These indicate that the complete protonated adenine system is not planar; however, the atoms of the imidazole ring are coplanar (plane 1), as are C(6) and its three bonded neighbours (plane 2). The fused-ring system is folded along the C(4)–C(5) bond and again along N(1)–C(5), as illustrated in Fig. 2. The imidazole ring is at an angle of 4·3° to the plane of the five atoms of the six-membered ring, excluding C(6) (plane 3), while plane 2 is at an angle of 5·3° to plane 3. These folds are in opposite senses with respect to plane 3. The fold about C(5)–C(6) and the distortions from planarity of the six-membered ring of the purine moiety have been noted in a number of other structures, but the deviations observed here are considerably larger than those reported earlier (see Sletten & Jensen, 1969; and Subramanian & Marsh, 1971). The fold about
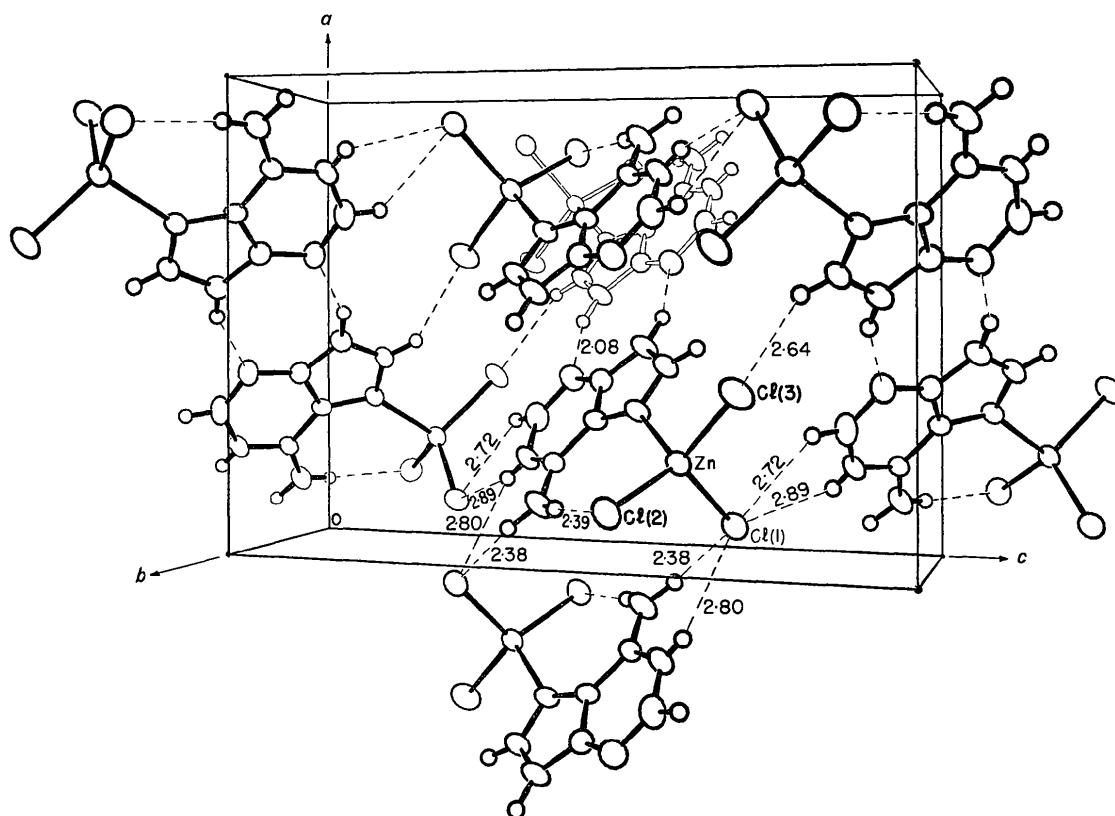

Fig. 3. A perspective view of the structure showing the unit-cell contents. Distances are noted for contacts shorter than 3 Å involving hydrogen atoms (dashed lines).

N(1)–C(5) brings N(6) closer to Cl(2) and thus strengthens the intramolecular hydrogen bond between N(6) and Cl(2), while at the same time retaining the co-planarity of the bonds about C(6).

No significance can be attached to the apparent deviations from planarity of the amino group in view of the large standard deviations in the hydrogen atom positions.

Table 3. *Final structure factors*

Data are listed in the order *l*, $10|F_o|$, $10|F_c|$, and 100σ ($|F_o|$) for each reflexion. Reflexions marked (*) were unobserved.

Table 4. *Equations of, and deviations (Å) from, various least-squares planes through atoms of the adenine moiety*

	Plane 1	Plane 2	Plane 3
q_a†	-0.6382	-0.6284	-0.6015
q_b	-0.6013	-0.5511	-0.5844
q_c*	0.4808	0.5429	0.5447
D (Å)	0.346	1.036	1.004
N(1)	0.180	0.001‡	0.004‡
C(2)	0.160	-0.063	-0.002‡
N(3)	0.071	-0.093	-0.005‡
C(4)	0.006‡	-0.043	0.009‡
C(5)	-0.003‡	0.001‡	-0.006‡
C(6)	0.063	-0.003‡	-0.038
N(7)	-0.002‡	0.119	0.091
C(8)	0.006‡	0.140	0.158
N(9)	-0.007‡	0.028	0.095
N(6)	0.032	0.001‡	-0.089
Zn	0.514	0.774	0.669
Cl(2)	-0.366	-0.128	-0.304
H(1)	0.23	0.02	0.00
H(2)	0.19	-0.11	-0.03
H(8)	0.00	0.20	0.22
H(9)	0.05	0.08	0.19
H(6–1)	-0.07	-0.03	-0.14
H(6–2)	-0.03	-0.11	-0.22

† q_a, q_b, q_c* are direction cosines with respect to **a**, **b**, and **c***, and D is the origin-to-plane distance.

‡ Indicates atoms which were included in the calculations with unit weight; all other atoms were given zero weight.

Hydrogen bonding

The molecules are linked in pairs by strong hydrogen bonds between N(9) and N(3) across the centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$ (Fig. 3). The two adenine ligands of a pair are coplanar; the point $\frac{1}{2},0,\frac{1}{2}$ being 0·02 Å from the least-squares plane through the atoms of the purine system. These pairs, in turn, are arranged in layers which lie parallel to (001), one layer near $z=0$, and another near $z=\frac{1}{2}$. Within layers, pairs of molecules are linked by hydrogen bonds between N(6) and Cl(1) (at $\bar{x}, 1-y, 1-z$) involving H(6–2). There is an intramolecular hydrogen bond N(6)–H(6–2)$\cdots$Cl(2). Data for these hydrogen bonds are given in Table 5.

Other intermolecular interactions of interest are all between chlorine atoms and hydrogen atoms. Both within layers and between layers, the major structural units (the pairs) are arranged in a manner that tends to maximize the number of chlorine–hydrogen interactions. Fig. 3 shows that the chlorine atoms lie close to the plane of the adenine ligands and that every hydrogen atom [except H(9)] is near one or two chlorine atoms. Cl(1) is surrounded by four hydrogen atoms, Cl(2) interacts with one, and Cl(3) is near three, although two of these three are about 3 Å away. These numerous chlorine–hydrogen interactions are indicative of the acidity of the hydrogen atoms of the protonated adenine moiety. The acidity of H(8) has been noted before (Sundaralingam, 1966) and in this case the Cl(3)–H(8) interaction of 2·64 Å is the only intermolecular contact less than 3 Å made by Cl(3). It might be described as a weak chlorine–carbon hydrogen bond. It is interesting that in this structure H(2) is also involved in reasonably close contacts with two chlorine atoms at distances of 2·72 and 2·80 Å; a weak interaction between the C(2) proton and oxygen has been noted in the crystal structure of adenosine (Lai & Marsh, 1972).

Conclusion

In addition to the structure described here, the structures of three other metal-containing compounds of purine nucleic acid bases with an N(9) substituent are now known: disodium adenosine triphosphate (Kennard, Isaacs, Motherwell, Coppola, Wampler, Larson & Watson, 1971); bis-(9-methyl-6-oxopurine)copper-(II) dichloride pentahydrate (Sletten, 1971); and dichloroaquo-(9-ethylguanine)zinc(II) (Taylor, 1972, unpublished results). In these, and in the title compound, N(7) is the sole site of attachment of the metal ion to the base. Two of the bases are protonated and two are neutral, indicating that N(7) is the primary site for metal–base interaction under a variety of conditions. Furthermore, none are chelate complexes involving the C(6) substituent, a possibility that has been discounted on steric grounds by Sletten (1971). This crystallographic information supports the conclusion of Shin & Eichhorn (1968), drawn from spectral evidence, that zinc(II) and copper(II) bind to the bases of DNA in a similar manner.

Table 5. *Hydrogen bond distances and angles, and data for some other intermolecular interactions involving hydrogen atoms*

Donor atom	Acceptor atom	Position of acceptor atom			Distances (Å) D$\cdots$A	H$\cdots$A	Angle (°)	
N(9)	N(3)	$1-x,$	$\bar{y},$	$1-y$	2·952	2·08	N(9)–H(9)—N(3)	156·6
N(6)	Cl(2)	$x,$	$y,$	z	3·226	2·39	N(6)–H(6–1)–Cl(2)	173·4
N(6)	Cl(1)	$\bar{x},$	$1-y,$	$1-z$	3·232	2·38	N(6)–H(6–2)–Cl(1)	149·5
N(1)	Cl(1)	$\bar{x},$	$1-y,$	$1-z$	3·447	2·80	N(1)–H(1)—Cl(1)	152·2
N(1)	Cl(1)	$\bar{x},$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$	3·378	2·89	N(1)–H(1)—Cl(1)	128·0
C(2)	Cl(1)	$\bar{x},$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$	3·391	2·72	C(2)–H(2)—Cl(1)	135·7
C(8)	Cl(3)	$1-x,$	$-\frac{1}{2}+y,$	$1\frac{1}{2}-z$	3·406	2·64	C(8)–H(8)—Cl(3)	143·7

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The Crystal Structure of α-Na₂Cr₂O₇ and the α–β Phase Transition

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α-Na₂Cr₂O₇ is triclinic, $A\bar{1}$, with $a = 7.82$ (3), $b = 10.36$ (3), $c = 9.54$ (3) Å, $\alpha = 89.5$ (3), $\beta = 110.1$ (3), $\gamma = 113.4$ (3)°, $Z = 4$. The structure has been refined ($R_2 = 0.054$) using 714 non-equivalent reflexions measured from precession photographs taken at 260 °C. The dichromate geometry is normal with a Cr–O–Cr angle of 135°. The structure is derived from that of β-Na₂Cr₂O₇ by a gradual displacement of the atoms in the crystal until the two crystallographically distinct layers become equivalent. The thermal vibrations of the dichromate ion indicate that it is undergoing large antisymmetric torsional vibrations, which are probably associated with the soft mode that causes the transition.

Introduction

In a previous paper (Panagiotopoulos & Brown, 1972a) we reported the crystal structure of the room temperature (β) phase of Na₂Cr₂O₇. Above 240 °C the crystal undergoes a displacive phase transition to α-Na₂Cr₂O₇ in a way which does not destroy the crystal. We now report the crystal structure of the high temperature phase and comment on the nature of the phase transition.

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Experimental procedure

The single crystal of β-Na₂Cr₂O₇ used for this work was prepared by the method described by Panagiotopoulos & Brown (1972a) and was sealed in a thin-walled quartz capillary tube in a nitrogen atmosphere.

The crystal and tube were heated in a hot air stream and the temperature, which was kept within a 5 °C range over the course of each photographic exposure, was monitored by a thermocouple set close above the crystal. The cell constants of the α phase, given in Table 1, were measured from precession photographs