

The Crystal Structure of Adenine Dihydrochloride*

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Adenine dihydrochloride, $C_5N_5H_5 \cdot 2HCl$, crystallizes in the orthorhombic system, systematic absences $0kl$, $k+l=2n+1$ and $hk0$, $h=2n+1$ consistent with the space groups $Pnma$ and $Pn2_1a$, with crystal data: $a=13.480$ (6), $b=6.553$ (2), $c=9.390$ (3) Å, $Z=4$, $D_m=1.68$ (1), $D_c=1.67$ g cm⁻³. Intensities for 1043 independent reflections were collected on an automated diffractometer. A structural solution in space group $Pnma$ has been obtained by standard heavy-atom methods and refined by full-matrix least-squares calculations, based on F , to R values of 0.036 (excluding zeros) and 0.037 (including zeros). The final weighted R value and goodness-of-fit are 0.035 and 2.2, respectively. The analysis in space group $Pnma$ requires exact coplanarity of the adenine dication and the chloride anions. The crystal structure is dominated by a series of $N-H \cdots Cl^-$ hydrogen bonds and contains a weak $N(10)-H \cdots N(3)$ interpurine hydrogen bond. The interaction between atomic layers at $y = \pm \frac{1}{4}$ is principally electrostatic. The effects on the geometric parameters in the protonated adenine nucleus are compared for further protonation versus metal coordination at N(7).

Introduction

Our interest in coordination complexes of purines (Kistenmacher, Marzilli & Chang, 1973; Marzilli, Kistenmacher & Chang, 1973; Kistenmacher, Szalda, Marzilli & Chang, 1974) has led us to investigate the crystal and molecular structures of a number of purine anions (Kistenmacher, 1973) and cations (Kistenmacher & Shigematsu, 1974*a,b*). These studies have been directed towards deducing the influence of protonation, deprotonation, alkylation and metal coordination on the basic structural parameters in the purine. In this paper we present a structural analysis of adenine dihydrochloride and compare the effect on the protonated adenine nucleus of further protonation versus metal coordination at N(7) [trichloroadeninium-zinc(II), Taylor (1973)]. To our knowledge the only other structural study of a dipositive cation of adenine is 9-methyladenine dihydrobromide [Bryan & Tomita (1962); $h0l$ and $hk0$ projection data].

Experimental

Crystalline adenine dihydrochloride was obtained from a saturated solution of adenine in 6*N* hydrochloric acid. The crystals were monoclinic prisms, $[010]$ as the prism axis, which had a small but distinctive taper. The crystals decompose on exposure to air, and we found it necessary to coat them with a thin film of petroleum grease and seal them in thin-walled Lindeman glass capillaries. Oscillation and Weissenberg photographs indicated an orthorhombic lattice. The

observed systematic absences ($0kl$, $k+l=2n+1$; $hk0$, $h=2n+1$) were consistent with the centrosymmetric space group $Pnma$ or the non-centrosymmetric space group $Pn2_1a$. Unit-cell dimensions were derived from a least-squares fit to the 2θ , ω and χ settings of 14 reflections measured on a diffractometer; the density was measured by flotation. Complete crystal data are given in Table 1.

Table 1. Crystal data for adenine dihydrochloride

$a=13.480$ (6) Å	$C_5N_5H_7Cl_2$
$b=6.553$ (2)	M. W. 208.05
$c=9.390$ (3)	Space group: $Pnma$
$V=829.5$ Å ³	$Z=4$
$\mu=7.4$ cm ⁻¹	$D_m=1.68$ (1) g cm ⁻³
$\lambda(Mo K\alpha)=0.71069$ Å	$D_c=1.67$
	$F(000)=424e$

Intensity measurements were made on a Syntex $P\bar{I}$ computer-controlled diffractometer; the incident beam of the spectrometer was monochromatized by a graphite crystal. The prism axis of the data crystal (0.33 mm in length with a cross section 0.20×0.20 mm²) was tilted relative to the ϕ axis of the diffractometer. Intensity data were collected with $Mo K\alpha$ radiation by the $\theta-2\theta$ scan technique. Individual scan speeds were determined by a rapid scan at each Bragg peak, and the rate of scanning varied from a minimum of 2° min⁻¹ (hkl and $hk\bar{l}$ octants) or 1° min⁻¹ ($h\bar{k}l$ and $h\bar{k}\bar{l}$ octants) to a maximum of 24° min⁻¹. Three standard reflections were measured after every 100 data points during the course of the experiment, and their intensities showed no unusual fluctuations or decay with time. All 4670 reflections in the $+h$ -hemisphere out to $2\theta=55^\circ$ were surveyed including systematic absences and standards. Those reflections which had intensities less than zero were assigned F and $w(F)$ equal to zero. The reflections with intensities greater than zero were

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given observational variances based on the following equation:

$$\sigma^2(I) = S + (B_1 + B_2) (T_S/2T_B)^2 + (pI)^2,$$

where S , B_1 and B_2 are the scan and background counts T_S and T_B are the scan and individual background counting times ($T_B = \frac{1}{4}T_S$ for all reflections), and p was taken to be equal to 0.03 and represents the error proportional to the diffracted intensity (Busing & Levy, 1957). Intensities and their standard deviations were corrected for Lorentz and polarization effects, but not for absorption [$\mu = 7.4 \text{ cm}^{-1}$, $\lambda(\text{Mo } K\alpha) \text{ radiation} = 0.71069 \text{ \AA}$]. The intensities were placed on an approximate absolute scale by the method of Wilson (1942).

Solution and refinement of the structure

The presence of four formula units of adenine dihydrochloride per unit cell immediately raises the question of whether the molecules are distributed in general positions in space group $Pn2_1a$ or occupy special positions in space group $Pnma$ requiring mirror symmetry to be imposed on the adenine dication. While a purine derivative has never been crystallographically required to be perfectly planar (Voet & Rich, 1970, Appendix III), several considerations led us to pursue a structural solution in space group $Pnma$: (1) The presence of a very large 020 reflection, approximately 60% of $F(000)$, was indicative of large amounts of electron density separated by $b/2$. In space group $Pnma$ this would require the molecular planes of the diprotonated cations to be separated by 3.27 \AA which is exactly the mean distance between molecular planes reported by Bryan & Tomita (1962) in 9-methyladenine dihydrobromide. (2) If the space group is $Pn2_1a$ (point group $m2m$), the reflections in the $+h$ -hemisphere should break down into distinct sets (hkl and $hk\bar{l}$; $h\bar{k}l$ and $h\bar{k}\bar{l}$) if anomalous dispersion differences are measurable in our data set (Ibers, 1967). We do not believe that our neglect of absorption effects should invalidate this consideration; the absorption effects will be systematic in reciprocal space, while the anomalous dispersion effects will be random. A careful examination of our measured intensities showed only one reflection where measurements in individual octants differed by more than $4\sigma(I)$. (3) Statistical averages for the normalized structure factors (E^2 's) were more consistent with a centric than an acentric distribution. While these considerations were not taken as proof that the space group was $Pnma$, a structural solution has been obtained in this space group and the proposed model provides an excellent fit to the experimental data.

The x and z coordinates of the two independent chloride anions were determined from a Patterson synthesis. A Fourier map based on the signs derived from the positions of the chlorine atoms ($R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.48$) revealed the positions of the remaining 10 heavy atoms in the asymmetric unit. Six cycles of isotropic least-squares refinement, minimizing

$\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, reduced R to 0.17. A difference Fourier map at this stage showed: (1) the positions of the seven hydrogen atoms in the asymmetric unit, and (2) that some of the atoms had somewhat large anisotropic components parallel to [010]; in particular, large components were indicated for Cl(2) and the exocyclic amine nitrogen N(10). These large components were attributed to a combination of packing effects and a possible incorrect choice of the space group (see below).

The refinement was continued, however, in $Pnma$, adding successively to the parameter list: (1) anisotropic thermal factors for the heavy atoms; (2) coordinates of the hydrogen atoms; (3) isotropic temperature factors for the hydrogen atoms. These final seven cycles of refinement were calculated on the basis of the 1042 symmetry-averaged reflections (assuming point group mmm) of which only three were zeros. The 020 reflection was excluded from these final cycles of refinement, $|F_o| = 256 e$, F_c about $-294 e$, the large difference being attributed to extinction effects. The final R indices are 0.036 (excluding zeros) and 0.037 (including zeros). The final weighted R value $\{[\sum \omega(F_o - F_c)^2 / \sum \omega F_o^2]^{1/2}\}$ and goodness-of-fit $\{[\sum \omega(F_o - F_c)^2 / (n - p)]^{1/2}\}$ for $n = 1039$ observations of non-zero weight and $p = 94$ are 0.035 and 2.2, respectively. The scattering curves for Cl, N, and C were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The scattering curve for H was that of Stewart, Davidson & Simpson (1965). The real part of the scattering curve for Cl was corrected for anomalous dispersion effects (Cromer, 1965). Final atomic coordinates and thermal parameters are given in Table 2. The final observed and calculated structure factor amplitudes were collected in Table 3. In the final cycle of refinement, no shift over error exceeded 1.0 for any parameter.

Discussion

Any detailed discussion of parameters derived on the basis of our model for the structure of adenine dihydrochloride must recognize that the model may be somewhat in error. Our analysis in $Pnma$ has provided an excellent fit to the experimental data at the cost of some atoms having large root-mean-square displacements normal to the mirror plane [Cl(2), $\text{RMSD}_{\text{min}} = 0.157 \text{ \AA}$, $\text{RMSD}_{[010]} = 0.312 \text{ \AA}$; N(10), $\text{RMSD}_{\text{min}} = 0.139 \text{ \AA}$, $\text{RMSD}_{[010]} = 0.276 \text{ \AA}$]. Large components normal to the mirror plane are expected if it is only an approximate and not a true crystallographic symmetry element. Furthermore, it is well known that purines generally show significant non-planarity in a crystalline environment (Sletten & Jensen, 1969; Voet & Rich, 1970). These displacements have usually been attributed to packing forces present in the crystal and in particular to the formation of out-of-plane hydrogen bonds. We have reason to believe (see below) that individual atomic displacements from the 'mean plane', if they exist in this structure, are less than 0.01 \AA .

Table 2. Final atomic parameters and their estimated standard deviations ($\times 10^5$ for the heavy atoms; $\times 10^3$ for the hydrogen atoms)

The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. $B_{12} = B_{23} = 0$.

	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₃
Cl(1)	30156 (4)	25000	94345 (6)	374 (3)	2269 (15)	652 (6)	83 (3)
Cl(2)	43573 (4)	25000	61028 (6)	286 (3)	4460 (24)	624 (7)	-38 (3)
N(1)	17585 (13)	25000	21117 (19)	305 (9)	2574 (53)	516 (18)	36 (10)
N(3)	2220 (12)	25000	33201 (19)	260 (8)	2773 (57)	716 (20)	-28 (11)
N(7)	20724 (14)	25000	59737 (18)	249 (9)	2280 (51)	574 (19)	-16 (11)
N(9)	4626 (13)	25000	58918 (19)	243 (9)	2318 (52)	656 (20)	91 (10)
N(10)	33124 (13)	25000	31554 (22)	257 (9)	3499 (68)	612 (21)	91 (12)
C(2)	7492 (16)	25000	21579 (24)	304 (10)	3048 (72)	583 (23)	-64 (13)
C(4)	7862 (14)	25000	45060 (21)	242 (9)	1630 (48)	596 (22)	21 (12)
C(5)	18069 (13)	25000	45584 (21)	233 (9)	1558 (47)	572 (21)	2 (11)
C(6)	23468 (14)	25000	32851 (22)	254 (10)	1765 (53)	594 (21)	5 (12)
C(8)	12537 (15)	25000	67470 (24)	333 (11)	2239 (60)	565 (22)	52 (13)

Table 2 (cont.)

	x	y	z	B
H(1)	206 (2)	250	124 (3)	3-1 (5)
H(2)	44 (2)	250	124 (3)	3-4 (5)
H(3)	-10 (2)	250	613 (3)	3-5 (6)
H(4)	125 (2)	250	778 (3)	2-7 (5)
H(5)	364 (2)	250	402 (3)	5-2 (7)
H(6)	356 (2)	250	241 (3)	3-1 (6)
H(7)	259 (2)	250	618 (3)	3-4 (6)

Such displacements should have a minimal effect on typical bond lengths (0.002 Å) and angles (about 0.1°) in the adenine dication. These estimated systematic errors are on the order of the random errors based on the positional standard deviations derived from the least-squares refinement (Table 2). We shall therefore confine our conclusions to differences that well exceed our estimated standard deviations.

Table 3. Observed and calculated structure factor amplitudes

The three columns contain values, reading from left to right, of I , 10F(obs) and 10|F(calc)|. The reflections designated with an asterisk had negative values for their net intensities and were assigned zero weight.

h	k	l	I	10F(obs)	10 F(calc)
0	0	0	1353	351	3 18 19
0	0	1	126	100	9 16 11
0	0	2	126	100	9 16 11
0	0	3	126	100	9 16 11
0	0	4	126	100	9 16 11
0	0	5	126	100	9 16 11
0	0	6	126	100	9 16 11
0	0	7	126	100	9 16 11
0	0	8	126	100	9 16 11
0	0	9	126	100	9 16 11
0	0	10	126	100	9 16 11
0	0	11	126	100	9 16 11
0	0	12	126	100	9 16 11
0	0	13	126	100	9 16 11
0	0	14	126	100	9 16 11
0	0	15	126	100	9 16 11
0	0	16	126	100	9 16 11
0	0	17	126	100	9 16 11
0	0	18	126	100	9 16 11
0	0	19	126	100	9 16 11
0	0	20	126	100	9 16 11
0	0	21	126	100	9 16 11
0	0	22	126	100	9 16 11
0	0	23	126	100	9 16 11
0	0	24	126	100	9 16 11
0	0	25	126	100	9 16 11
0	0	26	126	100	9 16 11
0	0	27	126	100	9 16 11
0	0	28	126	100	9 16 11
0	0	29	126	100	9 16 11
0	0	30	126	100	9 16 11
0	0	31	126	100	9 16 11
0	0	32	126	100	9 16 11
0	0	33	126	100	9 16 11
0	0	34	126	100	9 16 11
0	0	35	126	100	9 16 11
0	0	36	126	100	9 16 11
0	0	37	126	100	9 16 11
0	0	38	126	100	9 16 11
0	0	39	126	100	9 16 11
0	0	40	126	100	9 16 11
0	0	41	126	100	9 16 11
0	0	42	126	100	9 16 11
0	0	43	126	100	9 16 11
0	0	44	126	100	9 16 11
0	0	45	126	100	9 16 11
0	0	46	126	100	9 16 11
0	0	47	126	100	9 16 11
0	0	48	126	100	9 16 11
0	0	49	126	100	9 16 11
0	0	50	126	100	9 16 11
0	0	51	126	100	9 16 11
0	0	52	126	100	9 16 11
0	0	53	126	100	9 16 11
0	0	54	126	100	9 16 11
0	0	55	126	100	9 16 11
0	0	56	126	100	9 16 11
0	0	57	126	100	9 16 11
0	0	58	126	100	9 16 11
0	0	59	126	100	9 16 11
0	0	60	126	100	9 16 11
0	0	61	126	100	9 16 11
0	0	62	126	100	9 16 11
0	0	63	126	100	9 16 11
0	0	64	126	100	9 16 11
0	0	65	126	100	9 16 11
0	0	66	126	100	9 16 11
0	0	67	126	100	9 16 11
0	0	68	126	100	9 16 11
0	0	69	126	100	9 16 11
0	0	70	126	100	9 16 11
0	0	71	126	100	9 16 11
0	0	72	126	100	9 16 11
0	0	73	126	100	9 16 11
0	0	74	126	100	9 16 11
0	0	75	126	100	9 16 11
0	0	76	126	100	9 16 11
0	0	77	126	100	9 16 11
0	0	78	126	100	9 16 11
0	0	79	126	100	9 16 11
0	0	80	126	100	9 16 11
0	0	81	126	100	9 16 11
0	0	82	126	100	9 16 11
0	0	83	126	100	9 16 11
0	0	84	126	100	9 16 11
0	0	85	126	100	9 16 11
0	0	86	126	100	9 16 11
0	0	87	126	100	9 16 11
0	0	88	126	100	9 16 11
0	0	89	126	100	9 16 11
0	0	90	126	100	9 16 11
0	0	91	126	100	9 16 11
0	0	92	126	100	9 16 11
0	0	93	126	100	9 16 11
0	0	94	126	100	9 16 11
0	0	95	126	100	9 16 11
0	0	96	126	100	9 16 11
0	0	97	126	100	9 16 11
0	0	98	126	100	9 16 11
0	0	99	126	100	9 16 11
0	0	100	126	100	9 16 11

Bond distances and angles

An ORTEP (Johnson, 1965) drawing of the diprotonated adenine cation is shown in Fig. 1; interatomic distances are also given in this figure. Bond angles involving heavy atoms are presented in Table 4. Estimated standard deviations are about 0.003 Å for the heavy-atom bond lengths and about 0.2° for heavy-atom bond angles. Analogous values for the bond lengths and angles involving the hydrogen atoms are 0.03 Å and 2°.

The initiative for undertaking the structural analysis of adenine dihydrochloride has been to ascertain the effect on the structural parameters in protonated adenine of further protonation *versus* metal coordination at N(7), a site available and favorable for coordination in nucleic acid biopolymers. Taylor (1973) has recently reported the structure of trichloroadeniniumzinc(II) - protonated adenine coordinated to trichlorozincate(II) *via* N(7). These data, our recent refinement of the structure of adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974a), and the results reported here are compared in Table 4. As has been previously noted (Taylor, 1973; Kistenmacher & Shigematsu, 1974a), the bond lengths in protonated adenine do not seem to be affected by coordination at N(7). Inclusion of the data presented here for further protonation at N(7) does not seriously alter this conclusion. The only significant differences are in the bond lengths N(7)-C(8) and N(9)-C(8). In both monoprotonated adenine and the coordination complex, N(9)-C(8) is approximately 0.03 Å longer than N(7)-C(8). This difference has been reduced to about 0.01 Å in diprotonated adenine. This result is not particularly surprising since both N(7) and N(9) are protonated, and the imidazole ring should be approximately a symmetric resonance hybrid ignoring the asymmetry of the linkages at C(4) and C(5). The effects on the bond angles are more dramatic and approximately confined to the exocyclic and endocyclic

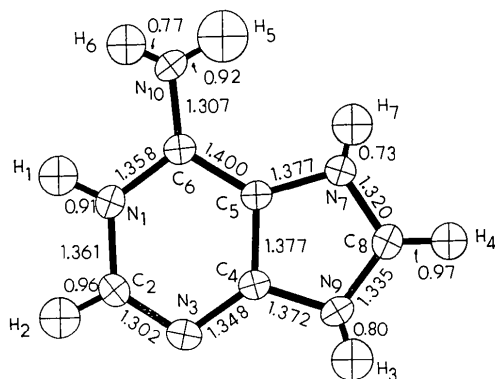


Fig. 1. Interatomic distances in the diprotonated adenine cation. Thermal ellipsoids are drawn at the 50% probability level (ORTEP, Johnson, 1965). The estimated standard deviation in the bond lengths is 0.003 Å, for those involving heavy atoms and 0.03 Å for those involving hydrogen atoms.

Table 4. A comparison of the heavy-atom bond lengths and angles in monoprotonated, diprotonated, and coordinated-protonated adenine

	Monoprotonated*	Diprotonated†	Coordinated-protonated‡
N(1)—C(2)	1.374 Å	1.361 Å	1.364 Å
N(1)—C(6)	1.360	1.358	1.363
N(3)—C(2)	1.289	1.302	1.283
N(3)—C(4)	1.358	1.348	1.360
N(7)—C(5)	1.377	1.377	1.385
N(7)—C(8)	1.320	1.320	1.313
N(9)—C(4)	1.360	1.372	1.350
N(9)—C(8)	1.351	1.335	1.343
N(10)—C(6)	1.311	1.307	1.302
C(4)—C(5)	1.377	1.377	1.379
C(5)—C(6)	1.403	1.400	1.415
C(2)—N(1)—C(6)	123.5°	124.0°	124.6°
C(2)—N(3)—C(4)	112.0	112.6	112.7
C(5)—N(7)—C(8)	103.1	108.3	104.2
C(4)—N(9)—C(8)	106.8	108.5	107.2
N(1)—C(2)—N(3)	125.1	124.9	124.8
N(3)—C(4)—N(9)	126.9	127.2	126.8
N(3)—C(4)—C(5)	127.8	126.4	127.1
N(9)—C(4)—C(5)	105.2	106.5	106.1
N(7)—C(5)—C(4)	111.3	107.1	109.5
N(7)—C(5)—C(6)	131.0	133.6	132.3
C(4)—C(5)—C(6)	117.7	119.3	118.1
N(1)—C(6)—N(10)	120.8	120.4	120.6
N(1)—C(6)—C(5)	113.8	112.9	112.6
N(10)—C(6)—C(5)	125.5	126.7	126.8
N(7)—C(8)—N(9)	113.6	109.7	113.0

* Adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974a). e.s.d.'s: 0.004 Å bond lengths; 0.2° bond angles.

† This study. e.s.d.'s: 0.003 Å bond lengths; 0.2° bond angles.

‡ Trichloroadeniniumzinc(II) (Taylor, 1973) e.s.d.'s: 0.008 Å bond lengths; 0.3° bond angles.

bond angles in the imidazole ring. In particular, there are significant differences in the following sets of angles: C(5)-N(7)-C(8) 103.1° and 104.2° monoprotonated and coordinated-protonated, 108.3° diprotonated; N(7)-C(5)-C(4) 111.3° and 109.5° monoprotonated and coordinated-protonated, 107.1° diprotonated; N(7)-C(8)-N(9) 113.6° and 113.0° monoprotonated and coordinated-protonated, 109.7° diprotonated. Each of the above differences appears to be consistent with the premise that protonation at N(7) has a delocalizing effect on the electron density in the imidazole ring, while metal coordination at N(7) invokes a smaller and more localized response.

Planarity of the adenine dication

The pseudoaromatic character of the purine fused-ring system generally restricts deviations from planarity to small values owing to the potential loss of resonance stabilization energy (Sletten & Jensen, 1969; Voet & Rich, 1970). In many cases where purines have been observed in crystalline structures, significant deviations from planarity have been noted and generally ascribed to crystal packing forces. Purines commonly show some bend about the C(4)-C(5) bond (Sletten & Jensen, 1969). Thus, the exact planarity required by our

analysis in *Pnma*, while theoretically possible, seems inconsistent with the majority of the data on purine systems. This consideration plus the large root-mean-square displacements normal to the mirror plane exhibited by some atoms indicates that the true space group is probably *Pn2₁a*.

It remains then to estimate the 'actual' non-planarity of the adenine dication and the effect of this non-planarity on the bond lengths and angles discussed above. We have rejected any attempt at assessing such displacements by least-squares refinement in the lower-symmetry space group *Pn2₁a* owing to the very probable ill-conditioned nature of the normal equations (Ermer & Dunitz, 1970; Donohue, 1971). Our estimate is based then on the following premise: The most planar purines are those in which non-bonded interactions are essentially coplanar with the purine ring system. We site in particular the planarity shown by the adenine framework in adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974*a*). In this structure, the largest deviation from planarity is about 0.01 Å [C(4), C(5) and C(8)]. The imidazole and pyrimidine rings are extremely planar (maximum deviation 0.002 Å) and the dihedral angle about the C(4)–C(5) bond is 52°. The planarity of the adenine framework is undoubtedly associated with the small deviations out of this plane shown by the chloride anion, –0.11 Å, and the hydrogen-bonded water molecule, 0.40 Å. The expectations are that the environment about the adenine dication in adenine dihydrochloride is as planar. We estimate then that the maximum deviation of any atom in the adenine framework is about 0.01 Å.

Crystal packing and thermal motion

(a) Hydrogen bonding

The crystal structure of adenine dihydrochloride is dominated by the layering of the atomic density perpendicular to [010] (Fig. 2). Within each layer there is an extensive array of hydrogen bonds and contacts (Fig. 2 and Table 5). Three of the hydrogen atoms on the adenine dication are involved in short H...Cl[–] hydrogen bonds: H(1)...Cl(1) 2.13 Å, H(5)...Cl(2) 2.18 Å, H(7)...Cl(2) 2.38 Å. The other two acidic nitrogen hydrogens, H(3) and H(6), participate in weak bifurcated H...Cl[–] hydrogen bonds: H(3)...Cl(1) 2.59 Å, H(3)...Cl(2) 2.70 Å; a weak interpurine hydrogen bond: H(6)...N(3) 2.34 Å; and a somewhat short contact, H(6)...Cl(1) 2.89 Å. As is found in the crystal structures of many purine cations, adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974*a*) for example, the hydrogen atoms attached to C(2) and C(8) are involved in contacts with electronegative acceptor atoms, here the Cl[–] anions (Table 5).

(b) Thermal motion and crystal packing

A projection of the structure down [010] is illustrated in Fig. 2. There is little molecular overlap of the adenine cations similar to the result found by Bryan & Tomita

Table 5. Distances and angles in the intermolecular contacts of the type D–H...A

D	H	A	D...A	A...H	∠D–H...A
Strong hydrogen bonds					
N(1)	H(1)	Cl(1 ^{iv})	3.033 Å	2.13 Å	170°
N(10)	H(5)	Cl(2 ^{iv})	3.106	2.18	178
N(7)	H(7)	Cl(2 ^{iv})	3.083	2.38	163
Bifurcated interactions and hydrogen bonds					
N(9)	H(3)	Cl(1 ⁱⁱⁱ)	3.313	2.59	152
N(9)	H(3)	Cl(2 ⁱⁱⁱ)	3.191	2.70	122
N(10)	H(6)	N(3 ^v)	2.924	2.34	132
N(10)	H(6)	Cl(1 ⁱ)	3.517	2.89	140
D–H...Cl [–] short contacts					
C(2)	H(2)	Cl(2 ⁱⁱ)	3.591	2.64	173
C(8)	H(4)	Cl(2 ⁱⁱⁱ)	3.258	2.75	113
C(8)	H(4)	Cl(1 ^{iv})	3.465	2.85	122
(i)	$x, y, -1+z;$	(iv)	x, y, z		
(ii)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z;$	(v)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$		
(iii)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z;$				

(1962) for 9-methyladenine dihydrobromide. This is not unexpected considering the relatively high charge on the cations in both structures. A point of particular interest is that the two independent chloride anions are located in quite different environments. In each case the in-plane interactions are similar, Fig. 2 and Table 5. However, in the out-of-plane direction, [010], the electrostatic potentials would seem to be very different. While Cl(1) sits nearly directly above (and below) C(5) of an adenine dication [Cl(1)...C(5), 3.29 Å], Cl(2) has as its closest contact the hydrogen atom off C(2) [Cl(2)...H(2), 3.29 Å]. It would seem then that Cl(1) should have a considerably stronger out-of-plane interaction with the adenine cations, *i.e.* Cl(1) should be sitting in a fairly well defined electrostatic potential. This difference in potentials is certainly

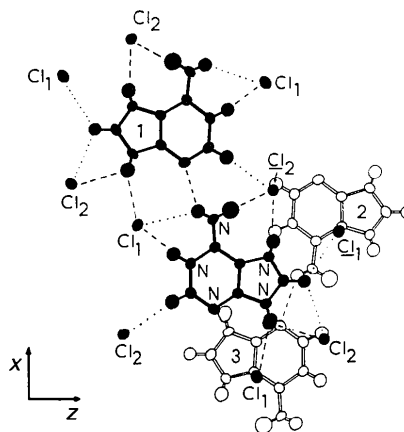


Fig. 2. A view normal to the *ac* plane of the crystal packing in adenine dihydrochloride. The shaded atoms have their centroids at $y = \frac{1}{4}$; the unshaded atoms have their centroids at $y = -\frac{1}{4}$. Hydrogen bonds are indicated by dashed lines; close contacts by dotted lines. The labeled adenine cation and the underlined Cl(1) and Cl(2) atoms have coordinates as given in Table 3. The adenine cations 1, 2 and 3 are related to the labeled cation by: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; $\frac{1}{2}-x, -y, \frac{1}{2}+z$; $-x, -\frac{1}{2}+y, 1-z$.

reflected in the moderate root-mean-square displacement for Cl(1) along [010] and a large component for Cl(2).

The structure factor and Fourier calculations were performed with the X-RAY 67 programs of Stewart (1967). The least-squares calculations were computed with a modified version of the ORFLS program of Busing, Martin & Levy (1962). All of the remaining computations were performed with locally written programs.

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The Crystal Structure of R_5Co_{19}

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Formation of the intermetallic compounds in the composition range 66–83 at. % Co of the R–Co intermetallic systems (R=rare earths) is described by the general formula RT_x where $x=(5n+4)/(n+2)$, $n=0, 1, 2, 3, 4, \dots$, T=transition metals Fe, Co and Ni. Using the structural data of the already known RT_x compounds for $n=0, 1$ and 2, simple mathematical relations are developed, with the help of which the lattice parameters and the atomic positions for any RT_x compound can be computed easily. Structural data for R_5Co_{19} are presented. It is shown that the structures of the RT_x compounds are the one-dimensional long-period superstructures of the $CaCu_5$ -type structure.

Introduction

Recently, a new compound having the formula R_5Co_{19} has been reported in the R–Co intermetallic systems for R=Ce, Pr, Nd and CeMM (Khan & Feldmann, 1973; Ray, Biermann, Harmer & Davison, 1973). The existence of this compound was first postulated by Cromer & Larson in 1959 on the basis of simple theoretical considerations. The arrangement of atoms in the structure of this compound is as yet unknown. Investigations were therefore carried out to determine the crystal structure of the R_5Co_{19} compound.

Experimental

Alloys (weighing 1–3 g) were prepared in the composition range RCO_3 – RCO_4 by arc-melting the constituents

on a water-cooled copper hearth under an atmosphere of purified argon. The purity of the elements was 99.9 wt. % for R and 99.99 wt. % for Co respectively.

Since the compounds in the above-mentioned composition range form peritectically (Khan, 1974; Ray *et al.*, 1973), the alloys were homogenized at 900°C for 7–14 days before further investigations. The structural changes were studied by annealing the homogenized alloy specimens at temperatures between 500–1150°C (depending upon the composition and the R element) for one day to three weeks (depending upon the annealing temperature) and subsequent quenching. In order to avoid oxidation of the specimens during heat treatment, they were wrapped in Ta foil and encapsulated in quartz ampoules filled with purified argon. The R–Co alloys for R=Ce were found to react with Ta foil above 950°C. In that case, alumina crucibles in-