Table 4. *Coordination*

Central atom	Coordinating atoms		Distances (±0·005)	Sum of atomic radii*
Cd(*f*)	4Ni(*e*)		2·86 Å	2·73 Å
	2Ni(*c*)	14	2·86	2·73
	4Cd(*f*)		2·97	2·98
	4Cd(*f*)		3·16	2·98
Ni(*c*)	6Cd(*f*)	12	2·86	2·73
	6Ni(*e*)		2·44	2·49
Ni(*e*)	3Ni(*e*)		2·54	2·49
	3Ni(*c*)	12	2·44	2·49
	6Cd(*f*)		2·86	2·73

* *International Tables for X-ray Crystallography* (1962).

References

Critchley, J. K. & Lott, R. J. (1963). *Nature, Lond.* **200** 773.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Lihl, F. & Buhl, E. (1955). *Z. Metallk.* **46**, 787.

Nevitt, M. V. (1962). *Electronic Structure and Alloy Chemistry of the Transition Elements*, p. 128. New York: Interscience.

Acta Cryst. (1965). **19**, 676

The Crystal Structure of Guanidinium Chloride

By D. J. Haas,* D. R. Harris and H. H. Mills†

Roswell Park Memorial Institute, Buffalo, New York, U.S.A.

(*Received* 6 *November* 1964 *and in revised form* 8 *March* 1965)

Guanidinium chloride, $C(NH_2)_3^+Cl^-$, crystallizes in the orthorhombic system with the space group *Pbca* and lattice constants:

$$a = 9{\cdot}18_4\,,\quad b = 13{\cdot}03_9\,,\quad c = 7{\cdot}76_5\ \text{Å}\quad (\text{all} \pm 0{\cdot}005\ \text{Å})$$

The crystal structure was solved by the heavy-atom method and refined by block-diagonal least-squares methods; the final R value is 0·062. The crystal structure consists of chloride ions coordinated by six nitrogen atoms of three different guanidium ions, two of which are nearly coplanar. The hydrogen bonds between the guanidium and chloride ions appear to be non-linear. The average carbon–nitrogen and chloride–nitrogen distances for the six coordinating nitrogen atoms are 1·323 and 3·303 Å respectively. The guanidinium ion is planar and has the molecular symmetry C_{3v}.

Introduction

The crystal structure of guanidinium chloride, $C(NH_2)_3^+Cl^-$, was determined in order to identify any structural similarities with those of the guanidinium chloride–*N,N*-dimethylacetamide complex (Haas, Harris & Mills, 1965). Even though the crystal structure of guanidinium chloride itself has never been determined, the structures of guanidinium bromide and iodide (Theilacker, 1935) and several other crystals containing the guanidinium ion and derivatives of guanidine have been published (Bryden, 1957).

Experimental

Crystals of pure guanidinium chloride were washed with acetone in order to round all corners and edges. A crystal in the shape of a prolate spheroid with dimensions 0·09 × 0·25 mm was chosen for the analysis. The space group and lattice constants were redetermined (Theilacker, 1931) and are given in Table 1.

Table 1. *Crystal data*

		(Theilacker, 1931)
Space group:	*Pbca*	*Pbca*
Lattice constants:	$a = 9{\cdot}18_4$ (±0·005 Å)	9·22
	$b = 13{\cdot}03_9$ (±0·005 Å)	13·06
	$c = 7{\cdot}76_5$ (±0·005 Å)	7·76
ϱobs:	1·35 g.cm^{-3}	1·35 g.cm^{-3}
ϱcalc: ($z = 8$)	1·365	

Three-dimensional intensities were collected (for $2\theta \le 150°$) on the General Electric XRD 5 with the Single Crystal Orienter using Cu $K\alpha$ radiation 'monochromatized' by Ni–Co balanced filters. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way. A total of 960 intensities were collected of which 287 were less than the minimum observable intensity. These reflections were not considered further in the analysis.

Determination of the crystal structure

The crystal structure was solved by the heavy-atom method. The coordinates obtained for the chloride ion from the three Harker lines of the three-dimensional

---

* Present address: U.S. Naval Research Laboratory, Washington, D.C., U.S.A.

† Present address: Chemistry Department, University of Glasgow, Glasgow, Scotland.

Patterson synthesis, $(U\,\frac{1}{2}\,0)$, $(0\,V\,\frac{1}{2})$, and $(\frac{1}{2}\,0\,W)$ were 0·000, 0·120, 0·179; for these coordinates, peaks were also present at $2x$, $2y$, $2z$ in the Harker sections arising from the twofold screw axes. Since the chloride ion does not contribute to two of the four structure factor groups (*International Tables for X-ray Crystallography*, 1952), an electron-density synthesis using the chloride ion phases revealed all the atoms of the guanidinium ion for both the true positions and the one related by the pseudo-mirror plane at $x=0,\frac{1}{2}$. It proved impossible to eliminate either of these groups on the basis of abnormally short interatomic distances. When structure factors were calculated for the groups to which the chloride ion does not contribute, the R value was greater than 0·60 for both models. This was reduced to 0·30 in both cases when the chloride ion was moved to $x=0{\cdot}020$, thus insuring that it contributes to all the intensity groups.

The correct structure was selected by performing one cycle of block-diagonal least-squares refinement on each arrangement of the guanidinium ion. The R values for the two structures after this refinement were 0·30 and 0·16. The latter was assumed to be correct and the details of the further refinement are shown in Table 2 (the least-squares refinement and R values employed unit weights and did not include the unobserved reflections).*

Table 2. *Progress of the refinement*

	R
One cycle of least squares with isotropic temperature factors	0·16
Four cycles of least squares with anisotropic temperature factors	0·081
Difference electron density synthesis to locate hydrogen atoms	
Structure factor calculation including the hydrogen atoms	0·073
Two cycles of least squares with anisotropic temperature factors and the hydrogen atoms (isotropic temperature factors) included in the refinement	0·062

The numbering system of the guanidinium ion is shown in Fig. 1 and the atomic arrangement in Fig. 2. The final parameters are listed in Table 3 along with the standard deviations of the positional parameters which were assessed in the usual way from the least-squares residuals. Table 3 also includes the hydrogen coordinates which were initially obtained from a difference electron-density synthesis and refined by least-squares in the final stages of the analysis. The interatomic distances and bond angles of the guanidinium ion and the chloride ion are listed in Table 4 (the values listed have not been corrected for thermal motion).

Discussion

The crystal structure consists of chloride ions coordinated by three different guanidinium ions, two of which are nearly coplanar (the standard deviation of the distances and the maximum distance from the

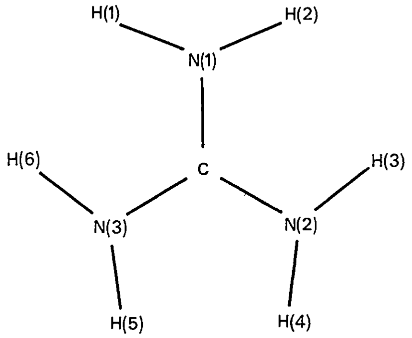

Fig. 1. Numbering system for the guanidinium ion.

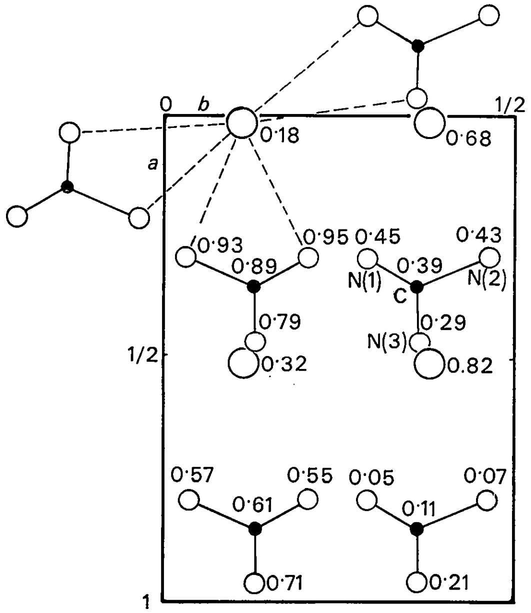

Fig. 2. Arrangement of the guanidinium and chloride ions in the unit cell.

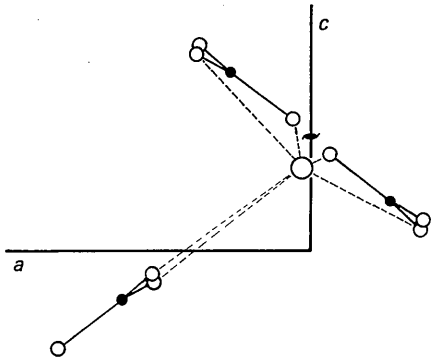

Fig. 3. Coordination of the chloride ion by three guanidinium ions viewed along the b axis. Two of the three guanidinium ions are nearly coplanar; the chloride ion 0·54 Å out of the plane.

---

* A 35 mm microfilm containing the observed and calculated structure factors has been deposited as Document number 8347 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, D.C. Microfilm copies can be obtained by an advance payment of $ 2·00.

'best' plane through the two ions are: 0·06 and 0·10 Å respectively). The third guanidinium ion is nearly perpendicular to this plane (Fig. 3). In addition to the electrostatic attractions, the chloride ion is assumed to be hydrogen-bonded to the guanidinium ions (it is 0·54 Å out of the plane in the direction of the third ion). The average chloride–nitrogen distance from the six nitrogen atoms is 3·303 Å with the second nearest nitrogen 3·92 Å from the chloride ion (Table 4). It can be seen, therefore, that each nitrogen coordinates two chloride ions; this is the best coordination that could be expected from packing considerations.

The guanidinium ion is planar to within the accuracy of the analysis (the maximum distance of an atom from the 'best' plane is 0·003 Å); the variation in the bond distances and angles for the ion is about one standard deviation and is not considered significant. This is in agreement with the fact that in two other structural analyses of guanidinium compounds, triaminoguanidinium chloride (Okaya & Pepinsky, 1957) and guanidinium gallium sulfate hexahydrate (Geller & Booth, 1958), the guanidinium ion lies on a threefold axis and therefore requires the bond lengths to be identical and the angles to be 120°.

The hydrogen positions determined from a difference electron density synthesis were given three cycles of least-squares refinement in which they showed relatively small shifts. Some of the hydrogen atoms are out of the plane of the guanidinium ion by as much as 0·2 Å, but since the coordinates of the hydrogen atoms are not accurate, these deviations may not be significant; a neutron diffraction study of urea (Worsham,

Table 3. *Coordinates* (Å) *and temperature factors of the atoms*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Cl	0·0203	0·0014	0·1187	0·0013	0·1823	0·0016	
C	0·3457	0·0054	0·3750	0·0057	0·3885	0·0054	
N(1)	0·2882	0·0033	0·2901	0·0088	0·4505	0·0054	
N(2)	0·2879	0·0055	0·4657	0·0047	0·4240	0·0054	
N(3)	0·4619	0·0035	0·3700	0·0088	0·2878	0·0052	
H(1)	0·3308	0·1	0·2398	0·1	0·3998	0·1	4·5
H(2)	0·2089	0·1	0·3000	0·1	0·5290	0·1	2·6
H(3)	0·2221	0·1	0·4610	0·1	0·4757	0·1	3·5
H(4)	0·3397	0·1	0·5147	0·1	0·3787	0·1	2·9
H(5)	0·4910	0·1	0·4504	0·1	0·2324	0·1	7·8
H(6)	0·4907	0·1	0·2860	0·1	0·2472	0·1	6·4
	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	
Cl	0·0112	0·0042	0·0207	0·0017	0·0041	0·0031	
C	0·0105	0·0044	0·0138	0·0010	−0·0014	0·0009	
N(1)	0·0138	0·0046	0·0206	−0·0020	0·0086	−0·0009	
N(2)	0·0144	0·0048	0·0224	0·0024	0·0103	0·0012	
N(3)	0·0139	0·0059	0·0209	0·0023	0·0115	0·0028	

Table 4. *Interatomic distances and angles*

C–N(1)	1·318 ± 0·006 Å	N(1)–C–N(2)	120·8 ± 0·8°
C–N(2)	1·325 ± 0·005	N(2)–C–N(3)	119·3 ± 0·8
C–N(3)	1·325 ± 0·006	N(3)–C–N(1)	119·7 ± 0·8
N(1)–H(1)	0·86 ± 0·1	H(1)–N(1)–H(2)	137·5 ± 5·
N(2)–H(2)	0·96 ± 0·1	H(3)–N(2)–H(4)	137·5 ± 5·
N(2)–H(3)	0·73 ± 0·1	H(5)–N(3)–H(6)	133·7 ± 5·
N(2)–H(4)	0·87 ± 0·1		
N(3)–H(5)	1·17 ± 0·1		
N(3)–H(6)	1·17 ± 0·1		
N(1)–Cl(6)*	3·272 ± 0·004	H(1)–N(1)–Cl	14·8 ± 5·
N(1)–Cl(8)	3·258 ± 0·004	H(2)–N(1)–Cl	14·2 ± 5·
N(2)–Cl(4)	3·246 ± 0·004	H(3)–N(2)–Cl	15·4 ± 5·
N(2)–Cl(6)	3·357 ± 0·004	H(4)–N(2)–Cl	12·2 ± 5·
N(3)–Cl(4)	3·350 ± 0·004	H(5)–N(3)–Cl	13·3 ± 5·
N(3)–Cl(8)	3·327 ± 0·004	H(6)–N(3)–Cl	20·1 ± 5·
H(1)–Cl(8)	2·44 ± 0·1		
H(2)–Cl(6)	2·36 ± 0·1		
H(3)–Cl(6)	2·66 ± 0·1		
H(4)–Cl(4)	2·41 ± 0·1		
H(5)–Cl(4)	2·23 ± 0·1		
H(6)–Cl(8)	2·27 ± 0·1		
Average C–N	1·323		
Average N–Cl	3·303		

* Asymmetric chloride ion in the general positions: (1) x,y,z; (2) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$; (3) $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (4) $\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$; (5) $-x$, $-y$, $-z$; (6) $\frac{1}{2}-x$, $\frac{1}{2}+y$, z; (7) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (8) $\frac{1}{2}+x$, y, $\frac{1}{2}-z$.

Levy & Peterson, 1957) placed the hydrogen atoms directly in the plane of the urea molecule, and the X-ray analysis of triaminoguanidinium chloride gave a similar result.

All the hydrogen atoms in this structure are off the nitrogen–chloride line of their respective nitrogen atoms. The average hydrogen–nitrogen–chloride angle is 15·0°; the individual angles are given in Table 4.

The two coplanar guanidinium ions that coordinate the chloride ion form a structural feature that is similar to the planes of guanidinium chloride perpendicular to the *a* axis found in the guanidinium chloride–*N*,*N*-dimethylacetamide complex. These planes of guanidinium chloride are held together by additional guanidinium chloride molecules acting as cross-ties. The coordination number of the chloride ion is nearly the same in both structures.

The authors wish to express their thanks to Drs D. Harker and J. Bello for many stimulating discussions and acknowledge the use of the IBM 1620 computer programs of Dr F. R. Ahmed, the block diagonal least-squares program by Y. Okaya & D. R. Harris, and the Fourier summation program, ERFR2, by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende. This work was supported by grants GM-09826 from the Institute for General Medical Sciences, NIH-A-3942 from the National Institutes of Health, NSF-GB-429 from the National Science Foundation, and a USPHS Traineeship, Training Grant 5T1GM-718-05 awarded to one of us (D.J.H.) through the Department of Biophysics, State University of New York at Buffalo.

References

BRYDEN, J. H. (1957). *Acta Cryst.* **10**, 677.
GELLER, S. & BOOTH, D. P. (1958). *Z. Kristallogr.* **111**, 117.
HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965. *Acta Cryst.* **18**, 623.
International Tables for X-ray Crystallography (1952) Vol. I. Birmingham: Kynoch Press.
OKAYA, Y. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 681.
THEILACKER, W. (1931). *Z. Kristallogr.* (A), **76**, 203.
THEILACKER, W. (1935). *Z. Kristallogr.* (A), **90**, 51, 256.
WORSHAM, J. E., LEVY, H. A. & PETERSON, S. W. (1957). *Acta Cryst.* **10**, 319.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1965). **19**, 679

The scattering length of yttrium for thermal neutrons.

BY M. G. PATON AND E. N. MASLEN, *Department of Physics, University of Western Australia, Nedlands, Western Australia.*

(*Received* 17 *February* 1965)

The scattering length of yttrium, b_Y, for thermal neutrons has so far been determined only from the scattering of its compounds, and the accuracy depends on the reliable knowledge of their structures. Neutron diffraction studies by powder methods on yttrium aluminum garnet, $Y_3Al_2(AlO_4)_3$, by Prince (1957), yttrium carbide, YC_2, by Atoji (1963) and yttria, Y_2O_3, by Villain (1957), Fert (1962) and Kuz'minov, Yamzin, Mal'tsev & Belov (1962) give the values listed in Table 1. The results for yttria range from $0{\cdot}71 \times 10^{-12}$ to $0{\cdot}816 \times 10^{-12}$ cm, and the extremes differ considerably from the other determinations. The yttria structure conforms to space group *Im*3, with eight metal ions at the special positions $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, and the remaining twenty-four at the sites $u,0,\frac{1}{4}$. The forty-eight oxygen ions are in general positions x, y, z. The largest value of b_Y by Kuz'minov *et al.* is based on an incorrect structural model conforming to space group $I2_13$ which was originally proposed by Zachariasen (1926, 1952). This determination is therefore rather suspect, and is ignored in the subsequent discussion. Villain and Fert used the neutron diffraction powder data to make least-squares analyses in which the four independent parameters and the yttrium scattering length were used as variables. A mean isotropic temperature factor coefficient was determined from a graphical comparison of the observed and calculated structure factors in the usual manner. The atomic coordinates from these analyses are listed in Table 2. The structure of yttria has recently been refined by X-ray methods using three-dimensional data from a single crystal (Paton & Maslen, 1965). The structural parameters, which are included in Tables 2 and 3, are considerably more accurate than those reported previously. In view of this a redetermination of the yttrium scattering length is warranted.

Table 1. *Scattering length of yttrium for thermal neutrons*

Authors	b_Y (cm × 10^{-12})
Prince	0·80 ± 0·01
Villain	0·71
Fert	0·79 ± 0·02
Kuz'minov *et al.*	0·816 ± 0·07
Atoji	0·786 ± 0·017
Paton & Maslen	0·781 ± 0·008
Best mean value	0·788 ± 0·005

Table 2. *Atomic coordinates for the yttria structure*

Author	*u*	*x*	*y*	*z*
Villain	−0·034	0·396	0·155	0·383
Fert	−0·0314 ± 8	0·389 ± 2	$0{\cdot}150 \pm 1_5$	0·377 ± 2
Paton & Maslen	−0·0328 ± 2	0·389 ± 1	0·154 ± 1	0·378 ± 1

A neutron diffraction pattern was recorded for this purpose using the powder spectrometer at the A.A.E.C. Research Establishment at Lucas Heights, New South Wales. The monochromatic beam, which was produced by reflex-