bond. This interaction and the packing in the chain can account for the departure of the angles around S from the tetrahedral value:

Cd–S–Cd	92·4°
Cd–S–C(1)	115·2
Cd–S $(\bar{x}, \bar{y}, z-1)$–C(1) $(\bar{x}, \bar{y}, z-1)$	102·0 .

Packing of the chains is determined by N $\cdots$ O(2) contacts involving two different $HCOO^-$ groups in adjacent chains.

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The Structure of the Crystalline Intermolecular Complex: Guanidinium Chloride–Disordered *N,N*-Dimethylacetamide (3:1)

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The crystalline complex guanidinium chloride–*N,N*-dimethylacetamide is monoclinic, space group $I2/a$, with lattice constants:

$$a=23{\cdot}47,\ b=14{\cdot}90,\ c=11{\cdot}95\ \text{Å};\ \beta=90{\cdot}95^\circ\ .$$

The crystal structure was solved by the heavy atom method and consists of a framework of guanidinium chloride with cylindrical cavities parallel to the c axis. The three guanidinium chloride molecules were refined by least-squares methods to an R value of 0·16. The disordered dimethylacetamide molecules lie in the cylindrical cavities (average diameter about 6 Å) that are continuous through the crystal.

Introduction

A program of study of the crystal structures of molecular complexes involving effective protein denaturants and model compounds has been undertaken in this laboratory in an effort to show specific interactions between protein denaturing agents and amino acid residue-like compounds. A number of these molecular complexes have been obtained; their significance has been discussed elsewhere (Bello & Haas, 1965).

Originally, it was expected that the complex of guanidinium chloride (GCl) with *N,N*-dimethylacetamide (DMA) would show interactions between the ions and the DMA, a proline residue analogue. After the crystal structure had been determined, however, it was apparent that no specific bonding could be attributed to the DMA molecules in the crystal.

Experimental

Crystals of the GCl–DMA complex were produced by saturating warm DMA (100 °C) with GCl and allowing the solution to cool slowly. Crystals used for the X-ray analysis were mounted in glass capillaries directly from this solution, while those used for the density determination and the chloride titration were first blotted dry on filter paper.

Titration for the chloride ion showed that the crystals contained 28% chloride by weight, which is consistent with the presence of 76 wt. % guanidinium chloride.

The density of the crystals was first taken in a kerosine–carbon tetrachloride gradient density column. The crystals were found to be unstable in these nonpolar liquids, the density slowly increasing with time. An accurate density was obtained, however, by placing the crystals in pure DMA and increasing the density of the liquid by adding bromoform. The most reliable density obtained by this procedure was 1·18 g.cm^{-3}.

Preliminary X-ray crystallographic analysis showed that the crystals are monoclinic with the reflection conditions: $h+k+l=2n$ for hkl, and $h=2n$ for $h0l$; the lattice constants are given in Table 1. This information indicates that the space group can be either *I*2/*a* or *Ia*.

Table 1. *Lattice constants*

$a=23·47$, $b=14·90$, $c=11·95$ Å	(all ±0·01 Å)
$\beta=90·95°$	(±0·05°)
ϱ obs = 1·18 g.cm^{-3}	ϱ calc = 1·188 g.cm^{-3}

From the volume of the unit cell, density, and space group, the weight of the asymmetric unit is either 371 or 742 amu. Use of the titration data indicated that the asymmetric unit contains 3 GCl and 1 DMA or 6 GCl and 2DMA, for the space groups *I*2/*a* and *Ia* respectively. The smaller formula unit was accepted as being correct and the space group *I*2/*a* was used throughout the analysis (origin taken on the *a* glide). The refinement of the guanidinium chloride part of the structure established that this was the correct choice.

Three-dimensional X-ray intensities were collected to a resolution of 1·0 Å on the GE XRD 5 with Single Crystal Orienter with Cu $K\alpha$ radiation 'monochromatized' by means of Ni–Co balanced filters. (The average of the intensities decreased rapidly with increasing 2θ). The intensities were corrected for absorption (Furnas, 1957) and converted to $|F|^2$ in the usual way.

Determination of the crystal structure

The crystal structure was solved by the heavy atom method. The positions of the three chloride ions in the asymmetric unit were determined by interpretation of the Patterson function. Both unmodified and modified $|F|^2$ (to weight the chloride–chloride vectors) were used in the calculation of the Harker sections UOW and $\frac{1}{2}VO$. For each of the chloride–chloride vectors in these sections, the corresponding $2x$, $2y$, $2z$ peaks were located in the three-dimensional Patterson function for all three chloride ions.

Structure factors calculated with the three chloride ions were used for the first three-dimensional electron density synthesis (EDS); the *R* value for this calculation was 0·47. From this and a second EDS, all the guanidinium atoms were located. Only two peaks greater than 3 e.Å^{-3} appeared which did not belong to the guanidinium or chloride ions, even when the *R* value had been reduced to 0·23. These peaks lay in a large open region where we assumed the DMA molecule to be. A difference EDS at this time revealed only a number of small peaks grouped together near the previously mentioned two unexplained ones.

At this time a model of one half the unit cell was constructed; from this we could see large cylindrical cavities passing through the crystal parallel to the *c* axis (Fig. 1). It was reasoned that the DMA molecules might be disordered and held within these cavities by hydrogen bonds to the nitrogen atoms of the guanidinium ions. If this were so, the DMA molecules would be essentially in a liquid state. Scans of 2θ in non-crystallographic directions of crystals with little surrounding liquid gave curves with a single broad peak. Since the peak of these curves was always between 20 and and 30 degrees 2θ, it was decided to refine the guanidinium chloride atoms of the structure using only reflections with $2\theta \geq 30$ degrees and try to fit the DMA molecules to peaks obtained from another difference EDS. The refinement of the guanidinium chloride atoms alone for reflections with $2\theta \geq 30$ degrees gave an *R* value of 0·16. The coordinates and temperature factors for the guanidinium chloride atoms obtained from the least-squares refinement are given in Table 2; the difference map calculated after this refinement is shown in Fig. 2. As one would expect from the rapid fall off of the average of the intensities with increasing 2θ, the temperature factors are rather high, particularly for the guanidinium ion (II) which forms part of the surface of the cavity.

Table 2. *Coordinates of the atoms*

Atom	*x*	*y*	*z*	*B*
Cl(1)	0·0115	0·0927	0·1121	3·6
Cl(2)	0·1966	0·1385	0·1162	5·0
Cl(3)	0·5294	0·3440	0·0798	4·4
Molecule I				
C(1)	0·9749	0·3707	0·2349	4·3
N(1)	0·9803	0·4446	0·1727	5·1
N(2)	0·9684	0·2914	0·1857	4·7
N(3)	0·9756	0·3757	0·3475	5·3
Molecule II				
C(2)	0·8544	0·0287	0·1274	7·2
N(4)	0·8852	−0·0051	0·0470	7·1
N(5)	0·7989	0·0084	0·1347	9·0
N(6)	0·8793	0·0788	0·2091	8·0
Molecule III				
C(3)	0·3724	0·2830	0·1185	6·2
N(7)	0·3990	0·2534	0·0236	6·0
N(8)	0·3201	0·2558	0·1390	6·3
N(9)	0·4021	0·3276	0·1930	5·5

A copy of the observed and calculated structure factors can be obtained upon request from the authors.

Discussion

The crystal structure is a framework of guanidinium and chloride ions held together by electrostatic attractions with the DMA molecules filling the cylindrical cavities. Since the DMA molecules are not specifically bonded to the guanidinium or chloride ions, it seems more than likely that other compounds can be substituted for DMA in the preparation of similar crystals. Furthermore, an exchange of DMA for other compounds appears to be possible, since the cylindrical cavities are continuous through the entire crystal. Upon being exposed to the atmosphere, a single crystal quickly becomes a polycrystalline mass, then slowly changes to a white powder.

The chloride–nitrogen and carbon–nitrogen distances are reasonably close to those found in pure guanidinium chloride, even though the structure of the

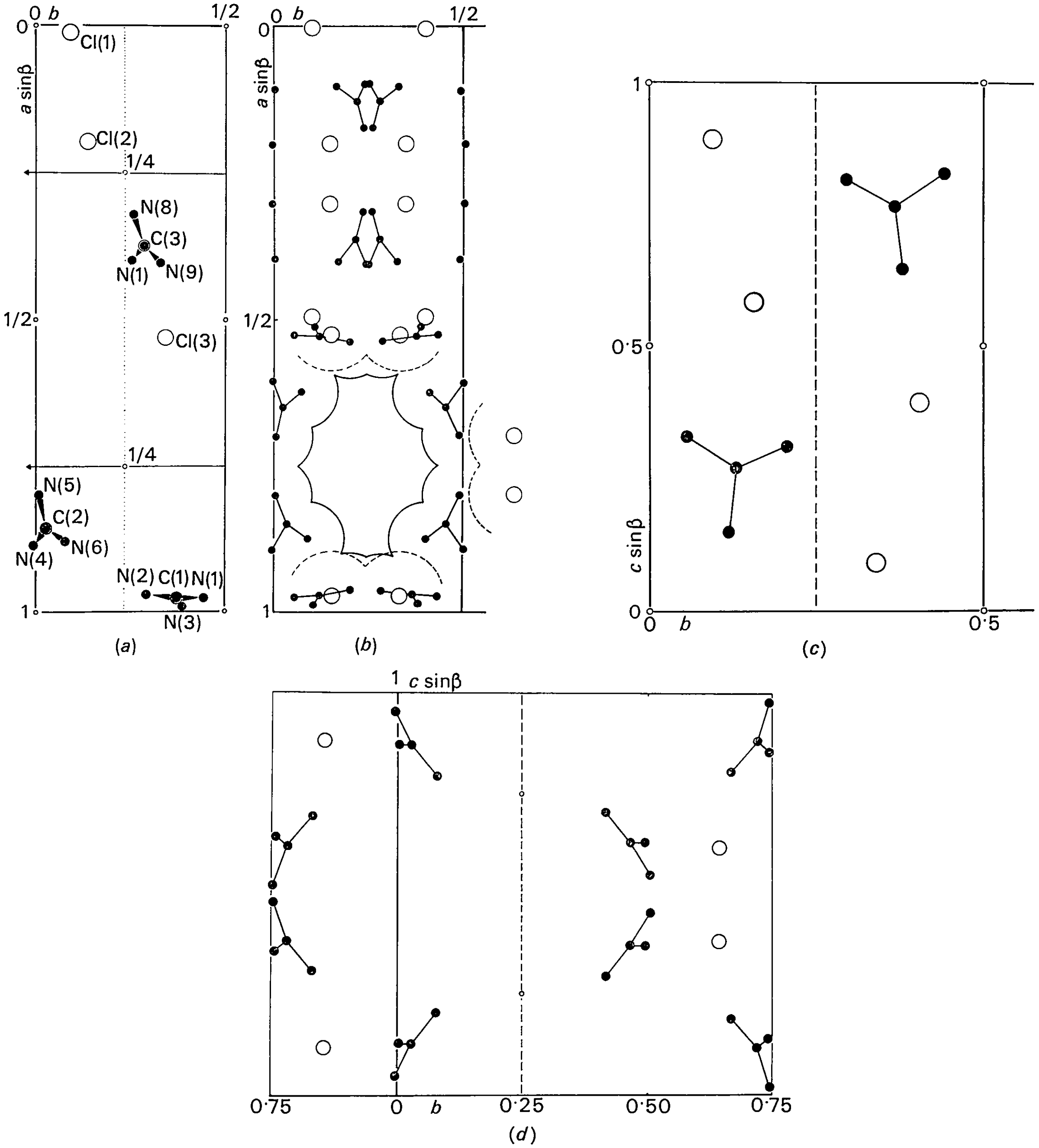

Fig. 1. (*a*) Atoms in the asymmetric unit ($z=0$ to 0·25) and symmetry elements that give one half the atoms in the unit cell; open circle–chloride ions, double circle–carbon atom, full circle–nitrogen atoms. (*b*) Half the unit cell in which can be seen the cylindrical cavity parallel to the *c* axis; outline of cavity is shown by full lines (projected van der Waals radii of the nitrogen–hydrogen atoms) and dashed circles (crystal radius of chloride ion). (*c*) Atoms with x coordinate between 0·45 and 0·55 projected on plane at $x=0·5$. (*d*) Atoms with x coordinate between 0·55 and 0·95 projected on plane at $x=0·75$.

complex could not be fully refined (Haas, Harris & Mills, 1965). These distances as well as the shortest chloride–chloride distances are given in Tables 3 and 4.

Table 3. *Interatomic distances and bond angles*

Molecule I		
C(1)–N(1)	1·34 Å	
C(1)–N(2)	1·33	(±.03)
C(1)–N(3)	1·35	
N(1)–C(1)–N(2)	119·9°	
N(2)–C(1)–N(3)	119·3	±(0·8)
N(3)–C(1)–N(1)	120·6	
Molecule II		
C(2)–N(4)	1·31 Å	
C(2)–N(5)	1·34	
C(2)–N(6)	1·35	
N(4)–C(2)–N(5)	120·4°	
N(5)–C(2)–N(6)	119·0	
N(6)–C(2)–N(4)	120·2	
Molecule III		
C(3)–N(7)	1·38 Å	
C(3)–N(8)	1·32	
C(3)–N(9)	1·30	
N(7)–C(3)–N(8)	119·3°	
N(8)–C(3)–N(9)	121·1	
N(9)–C(3)–N(7)	118·8	
Average C–N	$1{\cdot}33_5$ Å	
Average NCN angle	119·8°	

Table 4. *Chlorine–nitrogen distances* (<4 *Å*)

Cl	N	
1	2(I)*	3·25 Å
1	6(I)	3·34
1	3(II)	3·29
1	4(II)	3·37
1	7(II)	3·59
1	1(IV)	3·39
1	3(V)	3·28
1	4(V)	3·38
1	9(VIII)	3·29
2	5(I)	3·26
2	8(I)	3·39
2	4(II)	3·36
2	5(II)	3·72
2	7(II)	3·26
2	8(II)	3·53
2	8(VIII)	3·35
2	9(VIII)	3·32
3	3(I)	3·39
3	7(I)	3·40
3	9(I)	3·31
3	1(II)	3·37
3	2(II)	3·27
3	1(V)	3·54
3	2(VIII)	3·45
3	6(VIII)	3·48

Chlorine–chlorine distances (<4 Å)

Cl	Cl	
1	2(VI)	3·88 Å
1	3(VIII)	3·94
2	2(II)	3·77
3	1(VIII)	3·94

* Identify general positions (I) xyz, (II) $\frac{1}{2}-x, y, -z$, (III) $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$, (IV) $-x, \frac{1}{2}+y, \frac{1}{2}-z$, (V) $\frac{1}{2}+x, -y, z$, (6) $-x, -y, -z$, (VII) $x, \frac{1}{2}-y, \frac{1}{2}+z$ (VIII) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$.

The packing of the guanidinium and chloride ions is shown in Fig. 1. It can be seen that approximately one half of the unit cell is occupied by these groups; layers of guanidinium chloride parallel to (100) are present at $x=0, \frac{1}{2}$ (related by centers of inversion). Additional guanidinium and chloride ions act as cross ties between these layers.

The coordination of two of the chloride ions (Cl(1), Cl(2)) resembles that in pure guanidinium chloride in that two of the guanidinium ions coordinating each chloride ion are nearly coplanar. The chloride ion lies off this plane in the direction of one or more additional coordinating guanidinium ions. In the crystalline complex, the two nearly coplanar guanidinium ions form most of the inside surface of the cavity as can be seen in Fig. 1.

The average diameter of the cavities is about 6 Å, but the cavities are actually worm-shaped and have considerably larger regions (Fig. 1(*d*)).

Of the eight peaks greater than 0·5 e.Å^{-3} found in an asymmetric unit of the cavity, two of the three largest peaks are approximately 3 Å from neighboring nitrogen atoms; this suggests that they correspond to the oxygen atoms of the DMA molecules hydrogen bonded to these nitrogens. The rest of the peaks are believed to be due to statistical averaging over the preferred arrangements of the DMA molecules. Further refinement of this structure is not contemplated, because of the indeterminacy of the DMA arrangement.

The authors wish to thank Dr D. Harker for many stimulating disscussions and Dr J. Bello for giving us

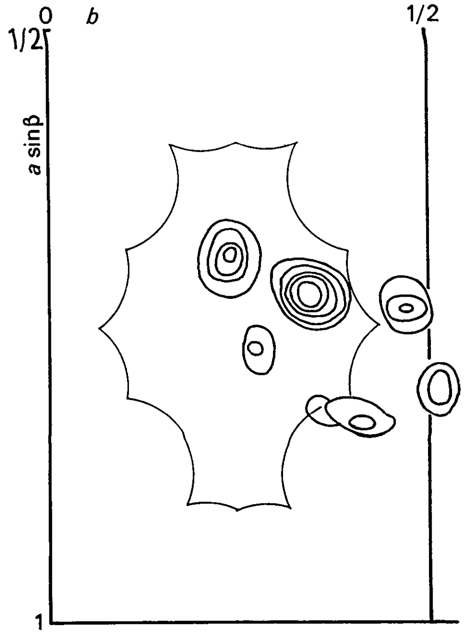

Fig. 2. Difference electron density map of the asymmetric unit showing peaks within the cylindrical cavity (contours at 0·5 e.Å^{-3} levels, zero contour omitted); projected van der Waals radii show their position in relation to the cavity (peaks outside these bounds lie below the guanidinium ions).

the crystalline sample for this investigation. In addition, we wish to acknowledge the use of the IBM 1620 computer programs of Dr F. R. Ahmed, and the Block Diagonal Least Squares Program by Y. Okaya and D. R. Harris. This work was supported by: USPHS grants GM-09826 from the Institute for General Medical Sciences and NIH-A-3942 from the National Institutes of Health, NSF-GB-429 from the National Science Foundation and a USPHS Traineeship, 2G-718(C2) awarded to one of us (D.J.H.) through the Department of Biophysics, State University of New York at Buffalo.

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The Crystal and Molecular Structures of *trans*-(1,4), (5,8)-Dimethylene-*cis*, *anti*, *cis*-perhydroanthraquinone

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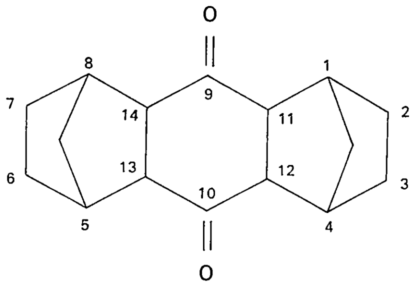
The crystal structure of *trans*-(1,4),(5,8)-dimethylene-*cis,anti,cis*-perhydroanthraquinone, $C_{16}H_{20}O_2$, *Pcab*, $a=10{\cdot}526$, $b=6{\cdot}464$, $c=18{\cdot}307$ Å, $Z=4$, has been solved directly from the normalized structure factor magnitudes with the use of the symbolic addition method. The structure has been refined in three dimensions. Analysis of the anisotropic thermal parameter data indicates that the major thermal vibration or disorder in the crystal is a rigid body molecular displacement in the direction of the crystallographic *b* axis.

Introduction

The compound *trans*-(1,4),(5,8)-*cis,anti,cis*-perhydroanthraquinone was prepared at the University of California, Los Angeles by deVries, Heck, Piccolini & Winstein (1959) as a starting material for the preparation of systems of interest in other investigations. Whereas the bonding configuration has been established by deVries *et al.*, the saturated carbon framework of the molecule allows considerable latitude of sterоconfiguration. In order to establish precisely this configuration, the compound has been subjected to X-ray crystal structure analysis.



(I)

The molecular configuration found from the crystal structure analysis is shown in Fig. 1, in which the numbering of the atoms is different from the conventional numbering shown in (I). The numbering shown in Fig. 1 is used hereafter.

Experimental

The sample from which a crystal was selected was synthesized and crystallized successively from ethyl alcohol, acetic acid, and *o*-xylene at the University of California, Los Angeles. It was dried at 110° *in vacuo.* The crystal used to collect all of the diffraction data was a small needle with a cross-section of several tenths of a millimeter. The crystal was mounted on its needle axis which is collinear with the crystallographic *b* axis.

The crystal is orthorhombic, space group *Pcab*, with unit-cell dimensions

$a=10{\cdot}526\pm0{\cdot}006$ Å
$b=6{\cdot}464\pm0{\cdot}003$
$c=18{\cdot}307\pm0{\cdot}012$
$V=1245{\cdot}7\pm1{\cdot}3$ Å^3
$d_c=1{\cdot}302$.
$d_o=1{\cdot}299$ (by flotation in aqueous sodium iodide).
$Z=4$.

The molecule must possess a center of symmetry since space group *Pcab* has eight equivalent general positi-

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