

The Structure of β -Tungsten Hexachloride by Powder Neutron and X-ray Diffraction

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β -WCl₆ is isostructural with UCl₆ and is hexagonal, space group $P\bar{3}m1$ (No. 164), with $a = 10.493$ (7) and $c = 5.725$ (4) Å. The positional parameters of tungsten were determined from the integrated X-ray powder intensities, while the chlorine parameters were determined from the neutron powder intensities by the profile-fitting technique. One tungsten atom W(1) lies in position 1(*a*) (000), and two tungsten atoms W(2) in positions 2(*d*), $\pm(\frac{1}{3}, \frac{2}{3}, z)$ with $z = 0.473$ (6). The chlorine atoms Cl(1), Cl(2) and Cl(3) all lie in positions 6(*i*) $\pm(x, \bar{x}, z)$, etc., with $x[\text{Cl}(1)] = 0.100$ (1), $x[\text{Cl}(2)] = 0.440$ (1), $x[\text{Cl}(3)] = 0.767$ (1), $z[\text{Cl}(1)] = 0.233$ (2), $z[\text{Cl}(2)] = 0.244$ (3) and $z[\text{Cl}(3)] = 0.304$ (2). The W atoms lie in octahedral holes in the hexagonal close-packed chlorine layers, and the octahedra around W(1) and W(2) are nearly regular. α -WCl₆, while having similar hexagonal close-packed chlorine layers, has a different arrangement of W atoms in the octahedral holes.

Introduction

Two polymorphs of WCl₆ are known. Ketelaar & van Oosterhout (1943) determined the structure of α -WCl₆ by single-crystal X-ray diffraction. α -WCl₆ is rhombohedral, with space group $R\bar{3}$ (C_{2v}^3), $a = 6.58$ (1) Å and $\alpha = 55.0^\circ$ (rhombohedral cell), or $a = 6.088$ (8) Å and $c = 16.68$ (15) Å (triple hexagonal cell). The three W atoms in the hexagonal cell are in positions 3(*a*) and the 18 chlorine atoms in positions 18(*f*) with $x = 0.295$ (5) and $z = 0.080$ (5). The crystal data are given in Table 1. α -WCl₆ (Fig. 1) consists of six hexagonal close-packed layers of chlorine atoms per cell, stacked perpendicular to the hexagonal *c* axis. Tungsten atoms at (000), $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ give a set of discrete WCl₆ octahedra. The chlorine atoms are attracted to the tungsten atoms, distorting the close-packed layers and giving a W-Cl distance of 2.24 Å in the octahedra. The octahedral holes containing no tungsten atoms are correspondingly expanded.

Although a phase change at 228°C had been observed by Liempt (1931), the structure of the second polymorph of WCl₆ was not investigated until recently (Smith, Lindingham, Smith & Johnson, 1968). These authors found a hexagonal polymorph of WCl₆ with $a = 10.511$ (3) Å and $c = 5.757$ (1) Å (Table 1), the cell being similar to that of UCl₆ which has the hexagonal space group $P\bar{3}m1$ and $a = 10.97$ and $c = 6.04$ Å (Zachariasen, 1948). By means of a calculation of the X-ray powder intensities, they showed that this form of WCl₆ and UCl₆ were isostructural. The hexagonal form is designated β -WCl₆ hereafter in this paper.

Since the atomic positions in β -WCl₆ have not yet been determined, and since β -WCl₆ is isostructural with the important compound UCl₆, a detailed examination of the structure of β -WCl₆ by neutron diffraction seemed worth while. This method was chosen in preference to X-ray diffraction as the neutron scattering

factors are more favourable, and absorption and extinction effects are negligible.

Experimental and results

Preparation and characterization

WCl₆ was prepared by direct synthesis from the elements at 800°C (Lietzke & Holt, 1950). The sample was rapidly cooled to room temperature. Any WOCl₄ in the preparation was removed by a sublimation. The lattice constants for this sample, determined by least-squares refinement of X-ray Debye-Scherrer powder diffraction data, were $a = 10.493$ (7) and $c = 5.725$ (4) Å, those of the β form. A small sample of β -WCl₆, with a larger crystal size than that prepared above, was formed by subliming WCl₆ slowly at 150°C in a N₂ atmosphere within a sealed tube. This observation suggested that the temperature of the phase change in WCl₆ was lower than the reported temperature of 228°C (Liempt, 1931).

α -WCl₆ was satisfactorily prepared using the method

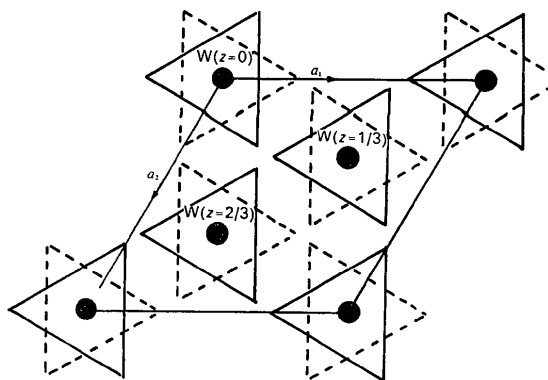


Fig. 1. The α -WCl₆ structure of Ketelaar & van Oosterhout (1943).

described by Ketelaar & van Oosterhout (1943). The lattice constants $a=6.088$ (4) and $c=16.68$ (1) Å for the α -WCl₆ triple hexagonal cell, determined as for β -WCl₆, were in agreement with those of Ketelaar & van Oosterhout (1943).

Neutron diffraction pattern and neutron refinement

The WCl₆ was packed into a 1 cm diameter vanadium can, using dry-box methods, and a neutron diffraction powder pattern was collected to $2\theta=41^\circ$ with $\lambda=1.082$ Å, using the elastic diffraction technique.

The unit-cell constants, determined from a least-squares refinement of 13 neutron line positions were $a=10.49$ (15) and $c=5.733$ (8) Å (Table 1). These cell dimensions were in agreement with those determined from the Debye-Scherrer pattern (Table 1). The cell dimensions of β -WCl₆ are smaller than those of UCl₆ ($a=10.97$ and $c=6.04$ Å), and this is consistent with the smaller 'size' of the tungsten atom, the ionic radii of W⁶⁺ and U⁶⁺ being 0.58 and 0.75 Å respectively (Shannon & Prewitt, 1969).

Since β -WCl₆ and UCl₆ are isostructural, the parameters suggested by Zachariasen (1948) for UCl₆ were used as the starting point for a least-squares refinement of the β -WCl₆ neutron diffraction data, using the profile-fitting technique of Rietveld (1967). The neutron scattering lengths (Neutron Diffraction Commission, 1972) were $b_w=0.48 \times 10^{-12}$ and $b_{Cl}=0.96 \times 10^{-12}$ cm. The refinement converged normally to a value of $\chi = \{\sum [w(I_o - I_c)]^2 / (NO - NV)\}^{1/2}$ of 1.26, and a value of $R = \sum (I_o - I_c) / \sum I_o$ of 0.115 over the individual points of the pattern. The observed and calculated neutron

diffraction profiles (Fig. 2) showed good agreement. Near the end of the refinement, a small excess of observed over calculated intensity was observed at $2\theta=22.5^\circ$ (Fig. 2). This was thought to be a peak arising from the 006 reflexion of α -WCl₆ impurity; the 006 structure amplitude for α -WCl₆ is $(18b_{Cl} - 3b_w)$, or 85% of the maximum value, $(18b_{Cl} + 3b_w)$. There appeared to be little additional interference from the probable small amount of α -WCl₆ impurity. To remove this effect, three data points near 22.5° were given small weights in the least-squares refinement in the final cycles. The three points are still included in Fig. 2 and in the above R value. The amount of α -WCl₆ present was probably only a few per cent, as the instrument is sensitive to small amounts of impurity.

X-ray refinement

Since the neutron scattering length b of tungsten (0.48×10^{-12} cm) is smaller than that of chlorine (0.96×10^{-12} cm) and there are six chlorine atoms for every W atom, the overall contribution of W in the diffracted neutron intensity was small. As a rough guide, the ratio $(b_w)^2 / (6b_{Cl}^2 + b_w^2)$ is only 4%, whereas in the X-ray case, the corresponding ratio is about 75%. It was therefore considered worth while to determine the parameter z -W(2) by a refinement of the X-ray powder data of Smith, Landingham, Smith & Johnson (1968). The observed X-ray intensities, I_o , of these authors were converted to $\sum JF_o^2$ values with the expression

$$\sum_j JF_o^2 \alpha I_o \sin^2 \theta \cos \theta (1 + \cos^2 2\theta)^{-1} A^*$$

Table 1. Crystal data for α -WCl₆ and β -WCl₆

	Formula weight = 396.57					
	a	c	U	D_m	Z	D_x Space group
α -WCl ₆ (a)	6.088 (8) Å	16.68 (5) Å	535.4 Å ³	3.520 g cm ⁻³	3	3.68 (2) g cm ⁻³ $R\bar{3}(C_{3i})$
β -WCl ₆ (b)	10.490 (15)	5.733 (8)	546.3	-	3	3.616 $P\bar{3}m1(D_{3d}^5)$
(c)	10.493 (7)	5.725 (4)				
(d)	10.511 (3)	5.757 (1)				

(a) Ketelaar & van Oosterhout (1943). (b) This work; neutron diffraction pattern. (c) This work; Debye-Scherrer pattern. (d) Smith, Landingham, Smith & Johnson (1968), Debye-Scherrer pattern.

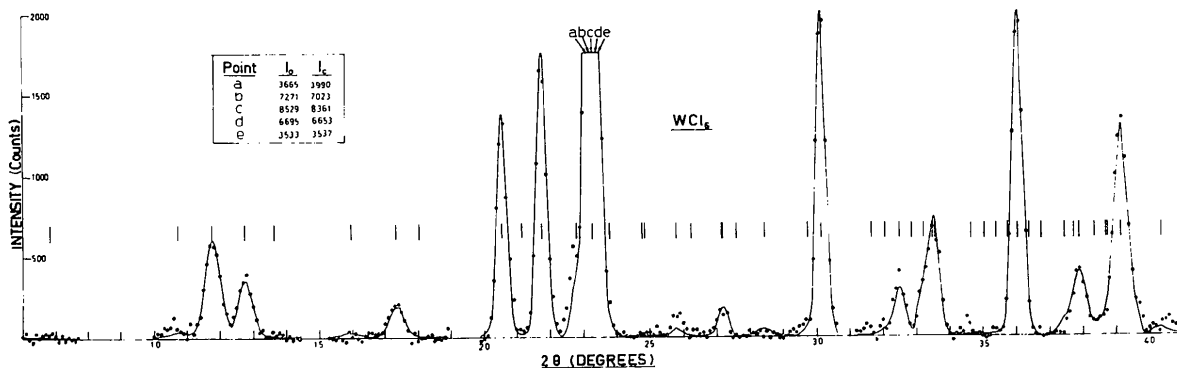


Fig. 2. Observed and calculated neutron powder patterns for β -WCl₆.

where each line consisted of j Bragg reflexions with multiplicities J . A^* was a cylindrical absorption factor, based on $\mu R = 18$, where μ is the linear absorption coefficient and R the capillary radius. The data to $2\theta = 56.3^\circ$ were used, and the positional parameters of W and Cl were refined, the function minimized being

$$\sum_i [w_i (\sum_j JF_o^2 - \sum_j JF_c^2)^2],$$

where i is the i th line in the pattern. The X-ray scattering curves for neutral W and Cl^- were used, uncorrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1962), and an overall isotropic Debye-Waller B factor was assumed. The chlorine parameters, as well as the single W parameter, refined satisfactorily, but the chlorine positional errors were larger than in the neutron refinement. The final value of the residual for the X-ray refinement,

$$\sum_i (\sum_j JF_o^2 - \sum_j JF_c^2) / \sum_i \sum_j JF_c^2$$

was 0.13.

There was reasonably good agreement between the X-ray and neutron chlorine parameters (Table 2). The X-ray W(2) parameter however, 0.473 (6), differed from the neutron parameter, 0.524 (8). A neutron refinement was carried out starting with a z -W(2) value of 0.473 (6), but the neutron parameter still refined to 0.524 (8). Since the X-ray data, for the reasons given above, were expected to give a much more reliable tungsten parameter than the neutron data, the value of 0.473 (6) was taken as the value for z -W(2). This value also gave a less distorted octahedron around W(2).

Table 2. Positional parameters ($\times 10^3$) in β -WCl₆ as found in this work compared with the idealized coordinates of Zachariasen (1948) for UCl₆

	x	y	z	Method
W(1)	0	0	0	
W(2)	$\frac{1}{3}$	$\frac{2}{3}$	473 (6)	X-ray
Cl(1)	100 (1)	-100 (1)	233 (2)	Neutron
	106 (12)	-106 (12)	228 (13)	X-rays
	100 (10)	-100 (10)	250 (20)	Ideal
Cl(2)	440 (1)	-440 (1)	244 (3)	Neutron
	435 (13)	-435 (13)	248 (14)	X-rays
	430 (10)	-430 (10)	250 (70)	Ideal
Cl(3)	767 (1)	-767 (1)	304 (2)	Neutron
	775 (6)	-775 (6)	329 (16)	X-rays
	770 (10)	-770 (10)	250 (20)	Ideal

$$\bar{B} = 2.5 (2) \text{ \AA}^2 \text{ (neutron)}$$

The final bond lengths and angles in β -WCl₆, based on the neutron Cl coordinates and the X-ray W parameter, are given in Table 3. The observed and calculated $\sum JF^2$ values for the X-ray refinement are given in Table 4.

Table 3. Interatomic distances and angles in β -WCl₆

W-Cl distances in octahedra (Å)		
W(1)-Cl(1) (6 ×)	2.26	(2)
W(2)-Cl(2) (3 ×)	2.34	(3)
W(2)-Cl(3) (3 ×)	2.23	(3)
Intralayer Cl-Cl contacts (Å)		
Cl(1)-Cl(1)	3.16	(4) (in octahedron)
Cl(1)-Cl(2)	3.67	(2)
Cl(1)-Cl(3)	3.70	(2)
Cl(2)-Cl(2)	3.36	(3) (in octahedron)
Cl(2)-Cl(3)	3.59	(2)
Cl(3)-Cl(3)	3.16	(3) (in octahedron)
Interlayer Cl-Cl contacts (Å)		
Cl(1)-Cl(1)	3.56 (3); 3.24 (2)	(in octahedron)
Cl(1)-Cl(3)	3.58 (2); 3.91 (2)	
Cl(2)-Cl(2)	3.66 (3); 3.55 (3)	
Cl(2)-Cl(3)	3.20 (2) (in octahedron); 3.66 (2)	
W-W distances (Å)		
W(1)-W(2)	6.77 (2); 6.64 (2)	
W(2)-W(2)	6.07 (1)	
Cl-W-Cl angles (°)		
Cl(1)-W(1)-Cl(1)	91.3 (7);	88.7 (7)
Cl(2)-W(2)-Cl(2)	91.6 (12)	
Cl(2)-W(2)-Cl(3)	89.0 (6)	
Cl(3)-W(2)-Cl(3)	90.3 (16)	

Discussion

The present analysis has provided measured parameters for β -WCl₆ in place of the ideal UCl₆ structure-type parameters of Zachariasen (1948). The measured and ideal parameters are compared in Table 2, and it is seen that the present errors are lower than those estimated for the earlier idealized model by a factor of 10.

Because of its tungsten arrangement, β -WCl₆ is not rhombohedral, like α -WCl₆, but primitive hexagonal (Fig. 3). In β -WCl₆, the atom W(1) lies at the origin [position 1(a) of $P\bar{3}m1$], while two W atoms, W(2), lie in positions 2(d), $\pm(\frac{1}{3}, \frac{2}{3}, z)$, with $z \approx 0.473$ (6). Approximately close-packed chlorine layers occur at $z \approx \frac{1}{4}$ and $\frac{3}{4}$,

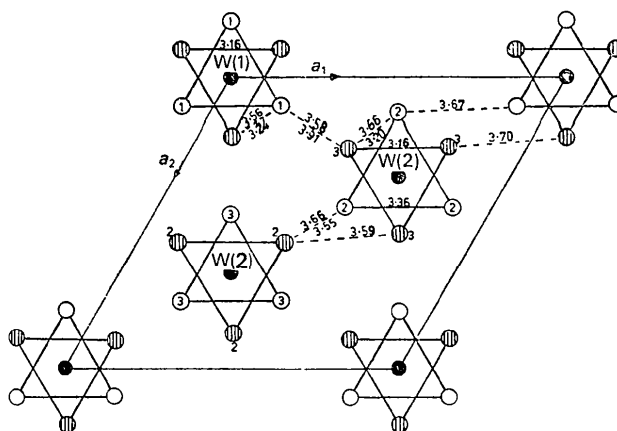


Fig. 3. The structure of β -WCl₆.

Table 4. Observed and calculated intensities ($\times 10^{-4}$) in the Debye-Scherrer X-ray pattern of β -WCl₆ (intensity data of Smith, Landingham, Smith & Johnson, 1969)

Where a reflexion of type hkl is given, the presence of $hk\bar{l}$, which occurs at the same angle but has a different F_c , is implied, and similarly for $h\bar{0}l$. Unobservably small intensities are denoted with an asterisk.

hkl	$\sum JF_o^2$	$\sum JF_c^2$
*100	0.7	0.0
*001	1.0	1.8
110	31.9	27.5
101	24.6	25.7
*200	1.3	0.0
111	4.0	4.1
201	19.8	19.6
*210	1.3	0.0
*002	1.3	0.0
*300	1.3	2.1
211	17.3	16.9
*102	1.3	0.0
301	26.4	27.6
220	8.8	9.0
{ 112		
{ 310	18.1	18.3
{ 202		
{ 221	4.7	5.3
311	19.0	20.7
*400	1.5	0.0
212	2.4	1.6
*401	1.5	4.5
{ 302		
{ 320	34.0	33.5
410	15.2	12.7
321	15.2	13.8
222	15.3	15.7
*003	1.6	0.0
312	4.2	4.3
{ 103		
{ 411	5.3	6.1
*500	1.6	0.0
*113	1.6	0.7
*402	1.6	0.6
203	5.3	4.1
330	21.7	20.6
*501	1.7	3.2
*420	1.7	0.0
*322	1.7	0.0
{ 213		
{ 331	16.7	16.7
421	5.4	8.7
{ 510		
{ 412	16.8	16.0

the Cl(1), Cl(2) and Cl(3) atoms all lying in positions $6(i)$.

The octahedron around W(1) is nearly regular, with Cl(1)–W(1)–Cl(1) angles of 91.3 (7) and 88.7 (7)° and a W(1)–Cl(1) distance of 2.26 (2) Å, essentially the same distance as in α -WCl₆ (2.24 Å) and WCl₆ vapour [2.26 (2) Å] (Ewens & Lister, 1938). The Cl(1)–Cl(1) edges are 3.16 (4) and 3.24 (2) Å, shorter than the usual ionic radius sum for the chloride ion (3.64 Å). The octahedron around W(2), for which different W(2)–Cl(2) and W(2)–Cl(3) distances are permitted, is also nearly regular, with W(2)–Cl(2) and W(2)–Cl(3) distances of 2.34 (3) and 2.23 (3) Å. The Cl–W(2)–Cl angles are also close to 90° in Table 3. The Cl(2)–Cl(2), Cl(2)–

Cl(3) and Cl(3)–Cl(3) distances in the octahedron around W(2) are also less than the ionic diameter of the chloride ion, Table 3. The W–Cl bonds in the structure appear slightly shorter than the ionic sum of W⁶⁺ and Cl[–] (Shannon & Prewitt, 1969). Although the radius ratio for WCl₆ (0.32), is in the range for tetrahedral coordination, octahedral coordination is observed in both α - and β -WCl₆.

As predicted by Zachariasen (1948) for UCl₆, the chlorine atoms are clustered around the metal atoms in WCl₆, Cl–Cl contacts not in an octahedron are about 0.5 Å longer than Cl–Cl contacts in an octahedron, Table 3 and Fig. 3, the latter set of distances being more nearly equal to the chloride ionic diameter.

β -WCl₆ appears to be the high-temperature form and α -WCl₆ the lower-temperature form of WCl₆. Liempt (1931) reported the transition temperature to be 228 °C, although experiments described in this paper indicate that this might be high. The higher density of α -WCl₆ (Table 1) is also consistent with its being the lower temperature form. α -WCl₆ would be expected to be slightly more stable than β -WCl₆ at room temperature because of its more symmetrical tungsten arrangement and larger W–W distances – all the W–W distances in α -WCl₆ are 6.58 Å, while the W–W distances in β -WCl₆ are 6.07, 6.61 and 6.80 Å (Table 3). The high-temperature form, β -WCl₆, may possibly be retained at room temperature by the fairly rapid quenching during the preparation.

The relation between the α - and β -WCl₆ cells is

$$\begin{aligned} \mathbf{a}_1(\beta) &= \mathbf{a}_1(\alpha) - \mathbf{a}_2(\alpha) \\ \mathbf{a}_2(\beta) &= \mathbf{a}_1(\alpha) + 2\mathbf{a}_2(\alpha) \\ \mathbf{c}(\beta) &= \mathbf{c}(\alpha)/3. \end{aligned}$$

Thus the index and coordinate transformations ($\alpha \rightarrow \beta$) are (1, –1, 0/1, 2, 0/0, 0, 0.333) and (0.667, –0.333, 0/0.333, 0.333, 0/0, 0, 3). It was found that the chlorine positions in α -WCl₆ transformed to the chlorine positions in β -WCl₆; that is, the chlorine layers are positioned in the same way relative to the threefold axis and mirror planes in both structures. The W positions in α -WCl₆ will not, of course, transform to the β -WCl₆ W positions. The difference between the polymorphs is essentially the different arrangement of W atoms in the octahedral holes. In α -WCl₆, the W atoms reside between every third layer of chlorine atoms, and in β -WCl₆ between every second layer. Transforming the rhombohedral indices ($-h+k+l=3n$) of α -WCl₆, it is seen that the present neutron reflexions would all have h and $k=3n$ if the W arrangement was of the α -WCl₆ type. The weaker reflexions, however, violate this condition.

It has been suggested (Canterford & Colton, 1968) that because WCl₆ is only moderately volatile (the vapour pressure is 11.4 kPa at 250 °C) the α -WCl₆ structure containing discrete octahedra is doubtful. However, the β -WCl₆ structure is similar in that it also contains discrete octahedra, so the involatility must be due

to other factors. The preparation described in the *Experimental* section has independently confirmed the existence of α - WCl_6 .

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Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components.

XIV. Crystal and Molecular Structure of the Amino Acid L-Cystine Dihydrochloride*

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A neutron diffraction study of L-cystine dihydrochloride, $\text{C}_6\text{H}_{12}\text{S}_2\text{N}_2\text{O}_4 \cdot 2\text{HCl}$, has been carried out. The structure is monoclinic, space group $C2$; $a = 18.595(6)$, $b = 5.243(2)$, $c = 7.231(3)$ Å, $\beta = 103.738(9)^\circ$; $Z = 2$. The structure has been refined by full-matrix least-squares techniques with a type II anisotropic extinction correction; the conventional R value is 0.034. All atoms have been located with a precision of better than 0.006 Å. The C–S–S–C torsion angle is $-81.7(2)^\circ$. Comparisons of the geometries of 15 molecules containing aliphatic C–S–S fragments show that the S–S and C–S bond lengths decrease as the magnitude of the C–S–S–C torsion angle increases from 0 to 90° . The L-cystine $\cdot 2\text{HCl}$ structure is stabilized by a three-dimensional network of one O–H \cdots Cl bond and three N–H \cdots Cl hydrogen bonds. Normal probability plots and χ^2 tests have been employed to compare atomic coordinates and temperature parameters from this study with those obtained in an independent neutron diffraction investigation [Gupta, Sequeira & Chidambaram (1974). *Acta Cryst.* **B30**, 562–567]. These comparisons indicate that there are significant differences between the two studies. The errors are normally distributed and pooled standard deviations are underestimated by a factor of 1.4–1.6.

Introduction

A neutron diffraction study of L-cystine dihydrochloride has been carried out as part of a series of investi-

gations of amino acids, small peptides, nucleosides and nucleotides. The aim of this work is to provide precise information about hydrogen-atom stereochemistry and hydrogen bonding in such systems.

The structure of L-cystine dihydrochloride has previously been studied by X-ray diffraction techniques (Steinrauf & Jensen, 1956; Steinrauf, Peterson & Jensen, 1958). After completing the present work, we learned of a similar independent study by Gupta, Sequeira & Chidambaram (1974).

Crystal data

L-Cystine dihydrochloride,
 $\text{C}_6\text{H}_{12}\text{S}_2\text{N}_2\text{O}_4 \cdot 2\text{HCl}$; F.W. 313.23.

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