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Structure of L-cystinediamide dihydrochloride.

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The crystal and molecular structure of L-cystinediamide dihydrochloride has been determined by three-dimensional X-ray crystallography using Cu radiation. The unit cell is orthorhombic with $a=17{\cdot}37$, $b=7{\cdot}50$, $C=5{\cdot}16$ Å and contains two molecules. The space group is $P2_12_12$.

The structure determination of L-cystinediamide dihydrochloride, $[SCH_2CH(NH_2.HCl)CONH_2]_2$, was undertaken to provide information concerning the observed anomalously high optical rotatory dispersion of this compound (Stapleton & Swan, 1962) and of cystine compounds in general. Equally important, studies of cystine structures could lead to information about the conformation and helical sense of the disulfide group in proteins under different environmental conditions.

Crystals of L-cystinediamide dihydrochloride (CDA) were obtained from Drs Ian Stapleton and Marvin Carmack (Indiana University, Bloomington). The crystals were, unfortunately, poorly formed and decomposed quickly. An irregularly shaped fragment with approximate dimensions $0{\cdot}03 \times 0{\cdot}03 \times 0{\cdot}01$ cm^3 was sealed inside a thin-walled glass capillary tube and three-dimensional data around the c axis ($l=0$–3) were collected with Ni-filtered Cu $K\alpha$ radiation to obtain reflections with spacings greater than 1 Å. A total of 378 non-zero independent reflections were measured using a Supper–Pace Autodiffractometer. The unit-cell dimensions were obtained from Weissenberg photographs with calibration lines from aluminum powder superimposed:

$a = 17{\cdot}37\ (0{\cdot}02)$ Å
$b = 7{\cdot}50\ (0{\cdot}02)$
$c = 5{\cdot}16\ (0{\cdot}02)$
$\varrho_{\text{calc}} = 1{\cdot}541$ g.cm^{-3}
$\varrho_{\text{obs}} = 1{\cdot}524$ g.cm^{-3} (flotation method)
Mol. wt. 311·3

Space group: $P2_12_12$ ($h00$ and $0k0$ absent for h or $k = 2n+1$). In the above mentioned space group, with two molecules in the unit cell, each molecule must possess a twofold symmetry axis. All previously determined cystine compounds which are able to possess a twofold axis have been found to do so. From the three-dimensional Patterson synthesis the positions of the chlorine atoms were easily obtained. A three-dimensional electron density map based only on the chlorine atoms gave the positions of all other atoms. The positions and temperature factors were refined by the block-diagonal least-squares method to an R index of 0·130 with the sulfur and chlorine atoms anisotropic and the other atoms isotropic. The structure was then refined further by the Busing & Levy full-matrix least-squares program modified foı mixed temperature factors.

Reflections were ordered on magnitude of F_o and grouped into blocks of 40 reflections each. The average F_o and $\Sigma(F_o-F_c)^2$ were found for each block. Weights w were then assigned so that $\Sigma w(F_o-F_c)^2$ would have the same value for each block. The final R index was 0·124, and the weighted R index, 0·144. The shifts in the final least-squares cycle were within 8% of its estimated standard deviations. The final positional and thermal parameters are listed in Table 1. The final bond lengths and angles with standard deviations are shown in Fig. 1. The conformation is shown by the stereoscopic drawing in Fig. 2 produced by Johnson's thermal ellipsoid plot program (Johnson, 1965).

All bond lengths and angles, except the S–C(1) bond and the S–C(1)–C(2) bond angle, were very close to those re-

Table 1. *Final positional and thermal parameters*

Atomic positions

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
Cl(I)	0·1590	0·0002	0·1974	0·0006	0·2014	0·0014
S	0·4998	0·0003	0·3633	0·0007	0·3621	0·0012
O	0·3242	0·0007	0·1729	0·0016	0·6011	0·0035
N(1)	0·3142	0·0007	0·4448	0·0018	0·2815	0·0043
N(2)	0·3621	0·0009	−0·0305	0·0024	0·3195	0·0042
C(1)	0·4354	0·0010	0·3116	0·0024	0·1104	0·0049
C(2)	0·3534	0·0008	0·2774	0·0024	0·1738	0·0042
C(3)	0·3466	0·0009	0·1389	0·0024	0·3940	0·0050

Thermal parameters

Estimated standard deviations are in parentheses.

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

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cl(I)	23 (2)	83 (10)	322 (65)	10 (3)	−8 (6)	−36 (14)
S	13 (2)	164 (12)	437 (70)	−5 (3)	9 (7)	93 (16)

Isotropic $T=\exp\left[-\beta(\sin\theta/\lambda)^2\right]$

	B
O	2·81 (0·31)
N(1)	2·57 (0·37)
N(2)	3·97 (0·40)
C(1)	2·57 (0·39)
C(2)	1·91 (0·38)
C(3)	2·02 (0·37)

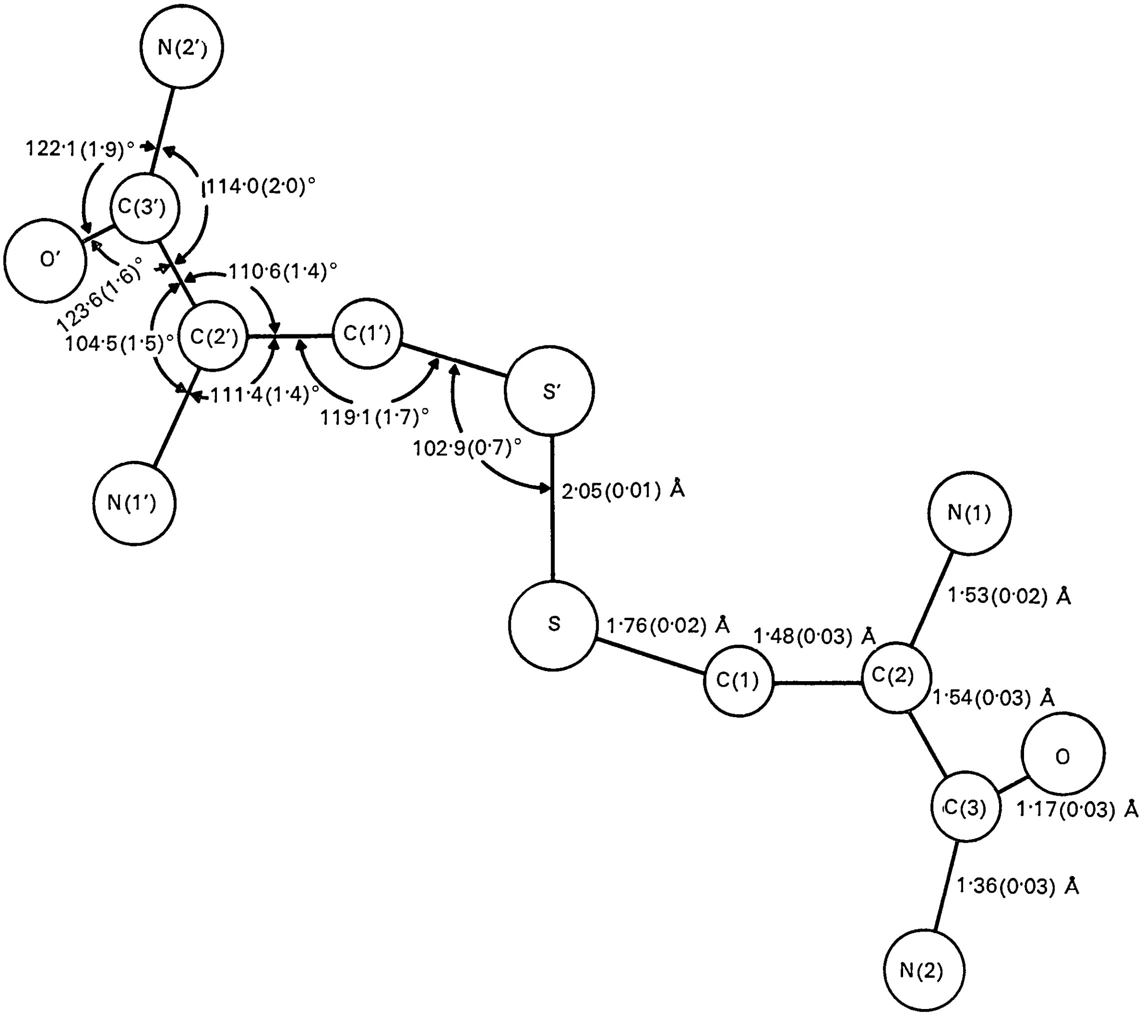

Fig. 1. Diagram of the molecule showing bond lengths and angles with the estimated standard deviations in parentheses.

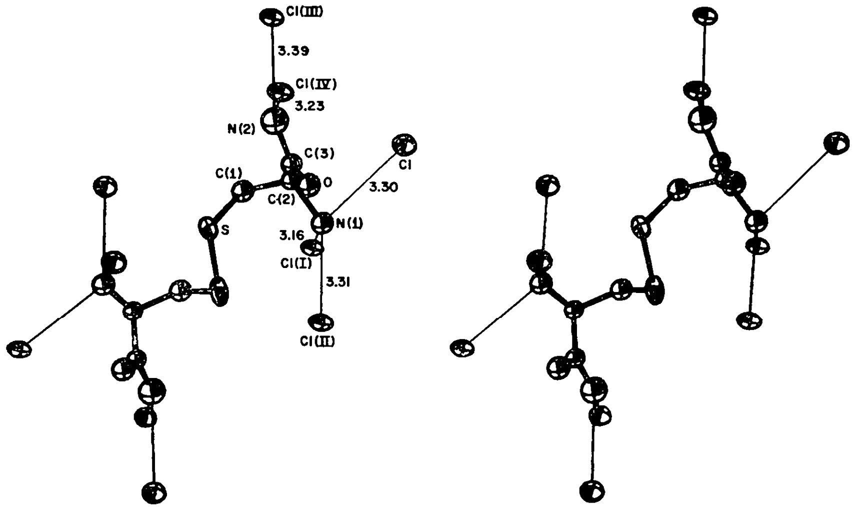

Fig. 2. Stereoscopic drawing produced by C. Johnson's *ORTEP* program (Johnson, 1965).

ported for other L-cystine compounds. The S–C(1) bond length of 1·76 (0·02) Å is approximately 0·08 Å shorter when compared with that of L-cystine dihydrochloride (Steinrauf, Peterson & Jensen, 1958), L-cystine dihydrobromide (Peterson, Steinrauf & Jensen, 1960), and *N,N*-diglycyl-L-cystine (Yakel & Hughes, 1954), and 0·04 Å shorter when compared with hexagonal L-cystine (Oughton & Harrison, 1957). This unusually short S–C(1) bond length may be the result of absorption errors and series termination errors due to the limited number of levels which could be collected.

After the refinement was completed it was recognized that the structure was isomorphous with L-cystine dihydrobromide which in turn is very similar to L-cystine dihydrochloride. It is quite interesting and rather unusual to replace the OH group with an NH_2 group and not alter appreciably the molecular packing. It appears that there may be slight differences in the coordinates of either the halide ion or the $OH(NH_2)$ group, since the NH_2 group in CDA forms two hydrogen bonds with halide ions while the OH group in the cystine hydrohalide forms only one hydrogen bond. This isomorphism of the cystine hydrohalide compounds and, in general, the amino acid hydrohalides may suggest that the packing of these molecules in crystals is largely controlled by their backbone conformation and to a smaller extent by their hydrogen bonding interactions. Of those compounds of L-cystine determined thus far, CDA, L-cystine dihydrobromide, L-cystine dihydrochloride, and *N,N*-diglycyl-L-cystine are all of one conformation and are characterized as having a left-handed helical sense. The conformation of hexagonal L-cystine is different, but related by rotations about the C(1′)–S′, S′–S, and S–C(1) bonds and characterized as having a right-handed helical sense.

The molecules of CDA are held together by a network of hydrogen bonds. The amino groups are charged and have chloride ions arranged in a rough tetrahedral manner about them. Although the N(1)–Cl distances, listed in Table 2, are slightly longer than the corresponding hydrogen bond distances reported for L-cystine dihydrochloride, they are still within hydrogen bonding distance. The neighboring oxygen atom, O(II), directly faces the amino nitrogen and does not participate in hydrogen bonding. The amide nitrogen, N(2), appears to form hydrogen bonds with two chloride ions. The N(2)–Cl(III) bond distance of 3·39 Å is slightly long and probably represents a weak hydrogen bond. The chloride ion, Cl(IV), lies very close to the plane of the amide group C(3), N(2), and O. The deviations of Cl(III) and Cl(IV) from the amide plane are 1·39 Å and −0·003 Å, respectively.

The C(1′)–S′–S–C(1) dihedral angle for CDA is 81·4°, which compares quite well with the values 80·2° and 81·3°

Table 2. *Intermolecular contacts less than* 4·0 Å.

Roman numerals indicate the relation of atom 2 to atom 1 at position *x,y,z*.

I	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\bar{z}$
II	$\frac{1}{2}-x$	$\frac{1}{2}+y$,	$1-z$
III	$\frac{1}{2}-x$	$-\frac{1}{2}+y$,	$\bar{z}$
IV	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$1-z$

Atom 1	Atom 2	Distance
N(1)	Cl	3·30 Å
N(1)	Cl(I)	3·16
N(1)	Cl(II)	3·31
N(1)	O(II)	3·01
N(2)	Cl(III)	3·39
N(2)	Cl(IV)	3·23

Table 3. *The final observed and calculated structure factors obtained with the atomic parameters in Table* 1. F_o, F_c, and α(°) are multiplied by 10.

h	K	F_o	F_c	α
Level ℓ = 0				
2	0	52	49	1800
4	0	408	453	1800
6	0	1363	1479	0
8	0	77	106	0
10	0	189	157	1800
12	0	608	584	0
14	0	308	320	0
16	0	100	99	0
1	1	463	383	0
2	1	236	176	0
3	1	382	401	0
4	1	118	93	0
5	1	442	479	0
6	1	210	196	0
7	1	39	66	0
8	1	83	101	1800
9	1	88	130	0
10	1	64	59	1800
11	1	314	310	0
12	1	55	57	0
13	1	160	144	0
14	1	157	151	1800
15	1	119	121	0
16	1	39	41	0
17	1	144	155	0
0	2	676	610	1800
1	2	369	331	1800
2	2	24	15	0
3	2	101	73	0
4	2	228	209	0
5	2	477	450	0
6	2	336	348	1800
7	2	229	235	1800
8	2	69	61	0
9	2	90	93	1800
10	2	238	255	0
11	2	189	215	0
12	2	233	263	1800
13	2	151	154	1800
14	2	123	103	1800
15	2	101	84	1800
16	2	131	130	0
1	3	689	566	1800
2	3	133	137	0
3	3	242	202	1800
4	3	294	265	1800
5	3	86	100	1800
6	3	99	72	0
7	3	428	433	1800
8	3	105	123	0
9	3	100	110	1800
10	3	110	123	1800
11	3	38	28	1800
12	3	48	53	0
13	3	342	371	1800
14	3	96	102	0
15	3	134	156	1800
0	4	174	166	1800
1	4	685	524	0
2	4	371	292	1800
3	4	78	72	1800
4	4	463	374	1800
5	4	572	512	1800
6	4	204	203	1800
7	4	354	337	0
8	4	158	148	1800
9	4	46	47	0
10	4	233	273	1800
11	4	134	158	1800
12	4	182	213	1800
13	4	162	186	0
14	4	100	98	1800
1	5	95	102	0
2	5	94	75	1800
3	5	363	303	1800
4	5	46	21	1800
5	5	106	86	1800
6	5	73	63	0
7	5	86	80	0
8	5	55	50	1800
9	5	276	293	1800
10	5	24	14	1800
11	5	109	138	1800
12	5	53	71	0
0	6	301	262	0
1	6	38	19	1800
2	6	39	25	0
3	6	62	33	0
4	6	33	14	1800
5	6	67	84	0
6	6	178	177	0
7	6	61	63	1800
8	6	25	13	1800
9	6	36	38	1800
10	6	28	23	1800
1	7	62	46	1800
2	7	115	92	1800
3	7	397	391	0
4	7	84	82	0
5	7	64	60	0
6	7	112	113	0
Level ℓ = 1				
2	0	54	107	1800
4	0	191	240	1800
5	0	156	180	2700
6	0	381	473	1800
7	0	149	168	2700
8	0	252	215	1800
9	0	386	419	2700
10	0	301	264	1800
11	0	174	96	2700
12	0	187	172	1800
13	0	64	62	2700
14	0	80	64	1800
15	0	339	388	2700
16	0	164	150	1800
17	0	143	125	2700
0	1	227	162	2700
1	1	673	586	2707
2	1	300	304	2246
3	1	505	511	2054
4	1	602	627	3108
5	1	411	460	1128
6	1	117	116	2825
7	1	224	245	2622
8	1	148	194	1586
9	1	288	314	2142
10	1	330	355	2896
11	1	351	336	1159
12	1	125	121	2452
13	1	59	35	1835
14	1	109	104	1855
15	1	195	199	2397
16	1	221	214	2887
0	2	335	223	1800
1	2	348	247	3134
2	2	612	494	2702
3	2	729	609	839
4	2	432	356	620
5	2	196	173	2550
6	2	44	39	2533
7	2	202	203	3005
8	2	192	220	2681
9	2	206	233	965
10	2	193	216	521
11	2	97	83	2098
12	2	39	16	600
13	2	39	20	2847
14	2	84	95	2242
15	2	122	120	922
16	2	52	45	456
0	3	118	101	900
1	3	209	159	1069
2	3	468	388	929
3	3	603	469	196
4	3	308	294	968
5	3	249	207	2826
6	3	83	48	2370
7	3	94	99	3529
8	3	225	219	876
9	3	363	396	286
10	3	203	246	900
11	3	153	176	2904
12	3	31	13	3484
13	3	65	66	2903
14	3	146	147	839
15	3	175	181	400
0	4	405	318	0
1	4	249	205	1255
2	4	342	286	671
3	4	292	231	1034
4	4	183	154	3029
5	4	227	184	905
6	4	317	272	3472
7	4	179	179	1109
8	4	270	266	622
9	4	130	130	725
10	4	131	156	2908
11	4	120	142	851
12	4	206	229	3185
13	4	150	170	847
14	4	206	207	535
0	5	292	226	900
1	5	229	201	3470
2	5	144	120	3351
3	5	112	88	1344
4	5	141	131	2173
5	5	106	98	74
6	5	268	246	1014
7	5	115	116	3290
8	5	104	103	384
9	5	83	91	1263
10	5	40	68	2515
11	5	63	70	3296
12	5	120	138	999
0	6	104	81	1800
1	6	84	73	1876
2	6	408	343	2734
3	6	242	221	2717
4	6	252	227	877
5	6	133	117	177
6	6	143	129	1405
7	6	40	36	1725
8	6	225	234	2610
9	6	175	153	2523
0	7	103	121	2700
1	7	121	172	2191
2	7	106	82	2478
3	7	86	62	1836
4	7	116	106	3275
5	7	72	75	1430
Level ℓ = 2				
2	0	166	187	0
4	0	218	256	0
5	0	275	343	900
6	0	390	471	1800
7	0	483	556	900
8	0	49	33	1800
9	0	235	231	900
10	0	144	127	0
11	0	191	163	900
12	0	162	135	1800
13	0	322	293	900
14	0	48	70	1800
15	0	107	105	900
16	0	79	54	0
0	1	187	192	900
1	1	396	399	2544
2	1	332	298	259
3	1	217	228	3239
4	1	300	362	1204
5	1	285	294	1344
6	1	232	277	1035
7	1	182	212	2638
8	1	213	206	134
9	1	107	108	3493
10	1	250	269	1164
11	1	241	228	1219
12	1	222	217	1151
13	1	51	35	2367
14	1	159	127	88
15	1	69	44	3276
0	2	75	104	0
1	2	110	94	983
2	2	131	120	2759
3	2	101	109	2902
4	2	121	99	2147
5	2	86	67	2383
6	2	165	158	268
7	2	86	77	2700
8	2	127	129	3084
9	2	48	61	3280
10	2	144	138	1720
11	2	112	114	2034
12	2	199	199	540
13	2	72	75	2778
14	2	116	107	3168
15	2	87	89	558
0	3	340	357	2700
1	3	318	309	438
2	3	138	124	2119
3	3	280	245	1686
4	3	199	173	3181
5	3	187	171	2981
6	3	392	403	2599
7	3	299	306	264
8	3	176	177	2502
9	3	132	124	1586
10	3	168	180	3017
11	3	119	124	2682
12	3	203	223	2601
13	3	160	178	76
14	3	98	63	2329
0	4	138	130	1800
1	4	331	312	2207
2	4	233	239	711
3	4	223	228	2641
4	4	147	133	3466
5	4	291	260	3177
6	4	104	94	2182
7	4	249	247	2342
8	4	135	139	904
9	4	168	175	2622
10	4	102	99	3427
11	4	176	171	3137
12	4	176	134	2703
13	4	175	176	2552
0	5	37	18	900
1	5	107	117	1883
2	5	205	211	2443
3	5	166	180	3451
6	5	120	108	1128
7	5	184	165	1599
8	5	113	108	2462
9	5	158	174	3137
10	5	136	134	3098
11	5	56	37	1070
0	6	63	57	1800
1	6	85	70	407
2	6	73	76	2447
3	6	32	38	395
4	6	26	10	1625
5	6	75	77	1584
6	6	77	68	1763
7	6	127	136	690
Level ℓ = 3				
1	0	139	212	2700
2	0	153	203	0
3	0	133	133	2700
4	0	252	289	0
5	0	37	5	900
6	0	72	97	0
7	0	217	198	2700
8	0	175	181	0
9	0	28	4	2700
10	0	360	316	0
11	0	32	33	900
12	0	67	32	0
13	0	320	258	2700
14	0	68	59	0
0	1	134	118	2700
1	1	215	188	860
2	1	235	179	3197
3	1	294	264	3449
4	1	208	207	1943
5	1	241	264	3071
6	1	101	74	2713
7	1	133	150	970
8	1	180	159	3313
9	1	179	160	22
10	1	134	105	1900
11	1	193	165	3443
12	1	131	87	2825
13	1	119	109	887
0	2	258	315	0
1	2	127	131	545
2	2	158	170	1416
3	2	110	115	2637
5	2	82	89	1748
6	2	155	180	3348
7	2	25	60	296
8	2	82	117	1006
9	2	94	96	2855
10	2	188	196	1771
11	2	37	27	2324
12	2	60	56	3098
13	2	77	70	490
0	3	287	298	900
1	3	39	46	2439
2	3	47	35	1923
3	3	375	337	1846
4	3	58	37	147
5	3	119	117	1175
6	3	193	185	745
7	3	39	59	1810
8	3	82	100	2427
9	3	284	310	1978
10	3	44	23	466
11	3	106	100	1390
12	3	167	143	763
0	4	206	219	1800
1	4	113	112	959
2	4	92	95	1822
3	4	74	59	693
4	4	89	71	1559
5	4	122	106	485
6	4	225	228	1510
7	4	127	119	1074
8	4	136	147	2195
9	4	82	70	1174
10	4	49	58	2390
2	5	145	128	1189
3	5	168	168	31
4	5	168	157	783
5	5	79	67	1753
6	5	101	85	3129
7	5	156	150	1822
8	5	134	128	1163

calculated for L-cystine dihydrochloride and L-cystine dihydrobromide, respectively; it is significantly different from the observed angle of 74° for hexagonal L-cystine. The interplanar distance between the almost parallel glycine-like groups for CDA is approximately 6·3 Å.

The equation of the mean plane through the atoms C(2), O, C(3) and N(2) is $0{\cdot}9507X+0{\cdot}1510Y+0{\cdot}2709Z+6{\cdot}402=0$. The maximum deviation from the mean plane for the above atoms is 0·03 Å. The amino nitrogen, N(1), which was not used in the mean plane calculation, deviates by 0·32 Å.

The final observed and calculated structure factors are given in Table 3.

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A note on the structure of $MoZn_{\sim22}$.*

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The powder data of Toussaint & Venker on the basis of which they assigned an orthorhombic structure to $MoZn_{\sim22}$ are explained better by assuming a f.c.c. structure with $a_0=18{\cdot}41$ Å.

In a recent paper Toussaint & Venker (1968) reported to have found a new type of intermetallic compound of approximate composition $MoZn_{22}$. They show a list of powder data, in which each reflection is indexed satisfactorily on the assumption that the structure is orthorhombic with $a_0=6{\cdot}510$, $b_0=10{\cdot}633$, $c_0=9{\cdot}205$ Å.

This author found that each of the published powder data can be explained by assuming a face-centered cubic lattice with $a_0=18{\cdot}41$ Å. The relationship between the edge lengths of the orthorhombic cell and the length of the cube edge is $6{\cdot}510\times2\times\sqrt{2}=10{\cdot}633\times\sqrt{3}=9{\cdot}205\times2=18{\cdot}41$ and the corresponding relationship between the indices is $h'^2+k'^2+l'^2=8h^2+3k^2+4l^2$, where the primed indices refer to the cubic and the unprimed to the orthorhombic lattice.

The advantages of indexing the observed powder lines on the basis of a cubic lattice with one parameter rather than a tetragonal lattice with two parameters ($a_0=6{\cdot}510\times\sqrt{2}$, $c_0=10{\cdot}633$ Å), an orthorhombic lattice with three parameters, or a triclinic lattice seem obvious: (1) The chances that the metric relationship between the cell edges of the noncubic lattice would be so exact as to preclude splitting of lines seem very small, especially since the observed lines seem to be very well defined as is indicated by the extremely good fit between observed and calculated $\sin^2\theta$ values. (2) Within the range of observation ($\sin^2\theta_{\max}=0{\cdot}4810$), there are 129 possible powder lines for the orthorhombic case, of which 42 would not be indexable on the basis of the face-centered cubic lattice. None of these 42 lines is observed. There are 93 possible powder lines for the cubic case, but only six of these (none present) are capable of ruling out the orthorhombic case.

It is interesting to note that in the cubic case, the strongest peak ($I/I_1=100$) corresponds to the 066 and 228 reflections. A characteristic feature of a series of other face-centered cubic structures having cell edges of lengths of the order of 18 or 19 Å, for example, $Cd_{\sim6}Ni$ and $Sn_{\sim4}Cu$ (Samson, unpublished), is the very high intensity of the 066 reflection.

The intermetallic compounds so far known to have the stoichiometry 1:22 are $ZrZn_{22}$ (Samson, 1961), $ReBe_{22}$ (Sands, Johnson, Zalkin, Krikorian & Kromholtz, 1962), and probably $MoBe_{22}$ and WBe_{22} (Paine & Carrabine, 1960). These are face-centered cubic but have cell edges of lengths of the order of 13 or 14 Å. It thus appears that $MoZn_{\sim22}$ represents a new type of cubic AB_{22} structure.

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