Acta Cryst. (1967). **22**, 75

The Structure of Bis-(*N*, *N*-dimethyldithiocarbamato)pyridinezinc

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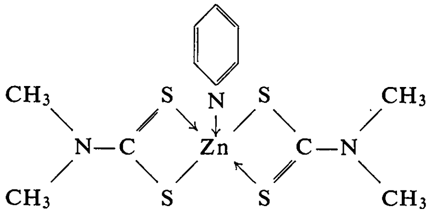
(*Received* 11 *May* 1966)

Bis-(*N*,*N*-dimethyldithiocarbamato)pyridinezinc crystallizes both with and without benzene of crystallization. The crystals with benzene, $C_5H_5N.Zn[S_2CN(CH_3)_2]_2.\frac{1}{2}C_6H_6$, are monoclinic, $P2_1/c$ with a = 12·67, b = 7·966, c = 20·13 Å, β = 105·27°. The structure has been solved with three-dimensional X-ray intensity data and the parameters refined until R = 0·085. The zinc atom is five-coordinate with a distorted trigonal bipyramid configuration, and has two long, axial Zn–S bonds of 2·60 Å, two shorter, equatorial Zn–S bonds of 2·33 Å, and an equatorial Zn–N (pyridine) bond of 2·08 Å. The dimethyldithiocarbamate groups are planar (excluding the hydrogen atoms) with a mean N–C bond length of 1·34 Å. The complex has approximately twofold symmetry. In the crystals without benzene the study of one projection has shown the molecules to be similar except for the orientation of the pyridine rings.

Bis-(*N*,*N*-dimethyldithiocarbamato)pyridinezinc (PZD_MC)



belongs to a group of five coordinate amine-dialkyldithiocarbamate zinc complexes which have been prepared by Higgins & Saville (1963). Some of these complexes are very active accelerators of the vulcanization of rubber by sulphur, and some have important biological properties. This analysis was undertaken to establish whether the zinc atom is five-coordinate and to determine the effect of amine coordination on the Zn–S and other bond lengths.

Two crystal modifications were encountered. Form A, obtained from benzene solution, was supplied by Dr B. Saville; a partial structure determination was carried out, but the crystals were poorly ordered and accurate stereochemical information could not be obtained. Subsequently crystals of PZD_MC, form B, containing benzene of crystallization, were obtained and an accurate three-dimensional study was made of these. The molecules of PZD_MC in the A and B crystals appear to be the same except for the orientation of the pyridine ring.

The structure of the A form

The large transparent plates, $C_5H_5N.Zn[S_2CN(CH_3)_2]_2$, decomposed slowly in air, losing pyridine, and were coated in collodion for X-ray photography. They are monoclinic, with space group Cc or $C2/c$.

a = 12·93 ± 0·03 Å $\quad$ D_m = 1·535
b = 8·94 ± 0·09 $\quad$ D_c = 1·563 g.cm^{-3}
c = 14·15 ± 0·03 $\quad$ Z = 4
β = 90·0°

With a cylindrical crystal, multiple-film Weissenberg photographs were taken, and the intensities of $h0l$ reflexions were estimated visually. Lp corrections and an absorption correction were applied. The high orders were very weak; only four reflexions were measured with $\sin\theta > 0{\cdot}70$. Attempts to record $hk0$ or $0kl$ data were even less successful.

The c-axis Patterson projection was consistent with the space group $C2/c$, in which Zn, N(1), and C(3) lie on the twofold axis. The sulphur atom positions were found from it and the carbon and nitrogen positions from an electron density projection. After refinement of these atomic positions R is 0·20. Work on these crystals was abandoned when the much better crystals of form B were obtained. Fig. 4 shows that the molecular shape is very similar to that in form B, except for the pyridine ring orientation.

Structure determination of the B form

Experimental

Fine transparent needles of

$$C_5H_5N.Zn[S_2CN(CH_3)_2]_2.\tfrac{1}{2}C_6H_6,$$

elongated along **b**, were obtained by dissolving the complex PZD_MC in an excess of hot benzene containing a few drops of pyridine, and allowing the solution to cool. They lose benzene readily on exposure to air, and were therefore sealed into thin walled glass capillary tubes for X-ray photography. Cell dimensions were measured from Weissenberg photographs about [010] and [101], calibrated with copper lines (a = 3·6150 Å). The space group is $P2_1/c$.

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$$a = 12{\cdot}670 \pm 0{\cdot}01\ \text{Å}$$
$$b = 7{\cdot}966 \pm 0{\cdot}005 \qquad \beta = 105{\cdot}27 \pm 0{\cdot}06^\circ$$
$$c = 20{\cdot}13 \pm 0{\cdot}02$$

The observed density, measured by flotation in aqueous potassium iodide, is 1·422 g.cm^{-3}, and the calculated density for $Z=4$ is 1·436 g.cm^{-3}. The discrepancy is presumably due to loss of benzene.

Using a nearly cylindrical crystal of diameter 0·144 mm and length 1·05 mm, the layers $h0l$ to $h4l$ were recorded on Weissenberg photographs with multiple films using Cu $K\alpha$ radiation and the intensities were estimated visually. 2267 independent reflexions were measured and another 444 were recorded as too weak to observe.

An empirical spot shape correction was applied as described by Harding & Cole (1963), and an absorption correction using the table for cylinders given by W. L. Bond (*International Tables for X-ray Crystallography*, 1959). The linear absorption coefficient is 57·0 cm^{-1}. Finally Lp corrections were applied. No good estimate could be made of the relative scales of the five layers; they were scaled later by comparison with $|F_{\text{calc}}|$.

Solution of the structure

The PZD$_{\text{M}}$C molecules are in general positions, but the benzene molecules lie across symmetry centres. The positions of the zinc atom and four sulphur atoms were found from a sharpened (010) Patterson projection. Most of the carbon and nitrogen atoms were found from Fourier series, and refinement of their positions reduced R to 0·23. The y coordinates of zinc and sulphur atoms were found from a sharpened (101) Patterson projection, and partly refined by Fourier methods. The zinc and sulphur coordinates were then used to calculate structure factors for all reflexions ($R=0{\cdot}40$), and the signs were used in a three-dimensional electron density series. All atoms, except hydrogen, appeared with reasonable electron densities.

Refinement

A three-dimensional (F_o-F_c) series was followed by seven cycles of least-squares refinement. Two very

Table 1. *Observed and calculated structure factors*

Each line is either h, k or l, $5|F_o|$, $5|F_c|$. Reflexions marked E appear to be considerably affected by extinction.

	0	0
2	419	-497
4	121	137
6	767	916E
8	243	-250
10	182	-181
12	18	-45
14	115	-111
16	54	-54
20	122	-100
24	52	54
	0	1
1	128	206
2	598	-637
3	287	-300
4	354	316
5	313	255
7	151	127
8	431	-439
9	480	-479
11	180	180
12	59	70
13	60	-57
14	218	-225
15	305	-308
16	161	159
17	79	82
19	45	-49
20	22	20
21	85	-77
22	84	74
23	22	21
24	12	23
	0	2
1	367	-404
2	224	198
3	358	323
4	495	-414
5	51	51
7	361	-326
8	167	155
9	18	15
10	21	9
11	35	17
12	33	-22
13	160	-164
14	113	108
15	153	-155
16	238	240
17	131	130
18	45	-52
21	54	-56
22	108	108
23	127	126
24	23	-31
	0	3
1	291	-339
2	125	-131
3	120	101
4	9	27
5	125	-111
6	402	371
7	297	-269
8	38	-39
9	274	259
10	117	-113
12	128	127
13	170	-183
14	104	108
15	267	276
16	74	-85
17	70	-70
19	27	29
20	20	35
21	45	50
22	19	-30
24	26	-27
	0	4
1	587	708
2	183	184
3	38	13
4	98	85
5	200	-206
6	218	-201
7	411	373
8	328	307
9	133	132
10	38	-37
11	45	-48
13	104	108
14	65	81
16	11	10
17	54	-57
20	42	-38
21	51	-52
22	35	38
23	31	-45
	1	0
-24	83	-71
-22	100	82
-20	108	82
-18	81	-83
-16	282	268
-14	236	-203
-12	232	-209
-10	415	433
-8	854	-1069E
-6	88	-71
-4	178	156
-2	525	-610
0	363	-467
2	472	580
4	39	55
6	383	-414
8	707	739
10	16	15
12	106	-76
14	245	243
16	115	-107
18	111	85
22	95	-85
24	34	23
	1	1
-24	88	89
-23	77	71
-22	27	-32
-19	64	-54
-18	39	27
-17	130	119
-16	89	-90
-15	107	104
-14	102	-100
-13	221	-235
-12	52	-68
-11	102	82
-10	185	-169
-9	268	268
-8	467	-470
-7	470	-475
-6	81	70
-5	104	-105
-4	140	-127
-3	763	962E
-2	367	-387
-1	282	-272
0	555	655E
1	457	450
2	325	384
3	291	253
4	224	-193
5	20	10
6	528	529
7	278	314
8	155	156
9	381	-367
10	168	-157
11	37	-37
13	252	254
14	102	85
16	229	-218
17	91	-80
19	98	82
21	15	33
22	124	-118
23	72	-64
24	44	42
	1	2
-25	38	51
-24	71	-70
-22	48	-55
-21	40	-43
-17	50	51
-16	162	-161
-15	230	-241
-14	15	-21
-13	13	-24
-12	31	46
-11	132	123
-10	142	-129
-9	276	-262
-8	89	84
-7	8	-17
-6	130	111
-5	61	53
-4	367	363
-3	237	224
-2	94	35
-1	466	-478
0	246	258
1	672	623
2	65	-57
3	409	352
4	99	123
5	43	-54
6	36	24
7	591	549
8	189	-196
9	154	-139
10	39	-51
11	47	42
12	17	25
13	244	258
14	310	-310
15	301	-316
18	36	31
19	60	62
20	80	-80
21	115	-116
23	38	-37
24	42	43
	1	3
-24	23	-27
-23	77	-88
-21	13	-23
-20	57	57
-19	22	-27
-18	49	-47
-17	76	-85
-14	236	238
-12	90	-91
-11	64	68
-9	97	-98
-8	156	159
-7	310	290
-6	188	-170
-5	120	-102
-4	9	9
-3	88	-86
-2	56	40
-1	656	717
0	22	-30
1	184	-191
2	258	230
3	148	-134
4	159	-169
5	766	688
6	157	-144
7	291	-277
8	224	227
9	156	-158
10	166	-169
11	67	77
12	164	-180
14	99	109
15	171	-185
17	46	55
18	22	-27
19	16	17
20	36	43
21	60	-66
23	65	77
	1	4
-23	65	-84
-19	72	73
-18	82	86
-17	112	-112
-16	142	-133
-15	189	177
-14	27	40
-13	83	81
-12	10	-22
-11	47	-49
-10	150	-138
-9	552	507
-8	78	74
-7	240	-221
-6	100	-83
-5	70	-67
-4	19	18
-3	405	385
-2	33	-16
-1	363	-372
0	57	-61
1	501	-468
2	217	-200
3	387	384
4	46	-31
5	194	-177
6	148	153
7	484	-433
8	188	-180
9	184	177
10	43	43
11	10	-13
12	165	162
13	109	-119
14	123	-124
15	64	69
16	75	75
19	89	74
21	43	47
	2	0
-24	125	-129
-22	58	-52
-18	145	-130
-16	53	-57
-14	91	84
-12	53	-50
-10	149	124
-8	509	535
-6	352	-311
-4	100	132
-2	623	814E
0	502	-632
2	54	-32
4	407	411
6	802	-880
8	216	-191
10	108	-111
12	157	-134
14	184	-167
16	59	33
18	105	88
20	62	-54
22	61	63
	2	1
-25	34	-23
-24	22	-22
-23	82	-68
-22	19	28
-21	78	65
-20	50	53
-17	220	-219
-16	197	196
-15	257	257
-14	84	87
-13	122	119
-11	473	-456
-10	361	372
-9	200	222
-8	173	-166
-7	106	105
-5	43	14
-3	408	402
-2	60	-97
-1	142	-148
0	507	-533
1	612	709E
2	23	-19
3	130	117
4	357	354
5	100	-106
6	614	-654
7	45	-42
8	456	453
9	238	228
10	26	24
11	137	-154
12	211	-203
13	98	-105
14	232	226
15	108	112
19	52	-43
20	82	79
21	40	32
23	53	57
	2	2
-25	35	-40
-24	62	60
-23	86	85
-21	38	-40
-19	26	-29
-18	58	60
-17	116	116
-16	52	-50
-15	78	76
-14	86	-92
-13	17	-26
-12	101	-101
-11	226	-212
-10	82	75
-9	365	358
-8	464	-437
-7	325	-315
-6	187	-199
-5	363	-331
-4	80	-50
-3	281	275
-2	212	-219
-1	254	-253
0	175	-166
1	64	41
2	656	579
3	151	129
4	100	-90
5	184	-176
6	193	201
7	30	46
8	173	165
9	68	48
10	47	-38
11	75	-76
12	112	122
13	15	-20
14	53	56
15	218	220
16	58	-63
17	67	-77
18	15	25
20	31	39
21	171	172
22	121	-123
23	80	-85
	2	3
-23	54	62
-22	61	-63
-21	65	58
-19	16	-29
-17	133	139
-16	164	-174
-15	92	-93
-13	53	-53
-12	157	161
-11	88	94
-10	208	-210
-9	472	-454
-8	87	77
-6	81	86
-5	75	86
-4	102	-79
-3	334	-312
-2	160	163
-1	290	-238
0	101	-91
1	343	320
2	191	177
3	43	53
4	370	336
5	405	-360
6	9	-12
7	585	561
8	85	82
9	109	109
10	175	189
11	89	-91
12	213	-224
13	294	289
15	28	-39
17	16	-25
18	55	-58
20	13	-28
21	56	-60
22	13	-23
	2	4
-23	15	-20
-22	21	-24
-21	85	-92
-18	15	31
-17	80	-84
-16	42	-44
-15	66	-80
-14	68	60
-12	42	-50
-11	160	-163
-10	110	101
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-5	225	-233
-4	102	76
-3	68	-72
-2	408	-366
-1	770	742
0	180	165
1	18	-20
2	71	70
3	147	-133
4	55	-47
5	503	453
6	75	65
7	55	-52
8	30	29
9	136	-144
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12	49	-48
13	8	-13
15	95	-93
16	41	-43
17	97	-92
18	9	-20
20	35	35
21	24	-25
22	32	-44
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-20	23	-32
-18	229	238
-16	215	-202
-14	35	36
-12	84	-75
-10	443	-456
-8	198	226
-6	41	-31
-4	427	-503
-2	765	1089E
0	671	745
2	51	7
4	18	57
6	626	659
10	182	-175
12	231	224
16	59	-57
18	83	-56
20	41	34
22	42	-37
	3	1
-25	85	78
-24	80	-71
-23	87	-74
-22	59	-56
-19	120	113
-18	140	-138
-17	173	-158
-16	114	-109
-15	155	-149
-14	100	-99
-13	134	120
-12	95	53
-11	140	-148
-10	197	-186
-9	245	-245
-8	273	274
-7	78	-77
-6	261	249
-4	229	-199
-3	457	-438
-2	899	1113E
-1	148	-148
0	157	-150
1	165	-157
2	69	58
3	186	154
4	559	527
5	138	109
6	73	-73
7	192	-190
8	247	-231
9	67	88
10	42	30
14	216	-215
15	72	-61
18	16	22
19	45	35
20	108	-99
21	72	-59
22	62	62
23	12	-18
	3	2
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-23	40	-44
-21	13	-21
-19	10	2
-17	185	-191
-16	186	179
-15	87	96
-14	117	115
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-11	217	-223
-10	185	184
-9	75	83
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2	104	-109
3	139	-140
4	24	-10
5	531	502
6	109	-110
7	332	-315
8	49	43
9	12	11
11	111	119
12	120	-124
13	411	-412
14	225	227
15	40	47
16	21	18
17	10	-8
18	48	-44
19	103	-108
20	103	111
21	18	23
22	41	45
	3	3
-24	22	24
-20	68	-64
-19	78	-77
-18	107	115
-17	52	57
-14	162	-171
-13	51	51
-12	189	196
-11	53	-54
-10	9	-8
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-7	131	-127
-6	43	-52
-5	252	-225
-4	22	-30
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-2	87	86
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0	109	-105
1	143	-134
2	198	-185
3	200	199
4	328	307
5	285	-258
6	33	40
7	203	-191
8	155	-157
9	98	102
10	62	73
11	113	-120
12	120	121
13	106	-110
14	9	-33
15	93	104
18	57	56
19	44	-50
21	97	107
	3	4
-23	72	88
-21	30	24
-19	41	-49
-18	70	-81
-17	192	188
-16	90	89
-15	50	-50
-13	22	23
-12	117	-120
-11	173	169
-10	160	156
-9	348	-322
-8	108	-110
-7	24	44
-6	39	30
-5	166	146
-4	21	-16
-3	607	-532
-2	42	48
-1	33	-38
0	29	-40
1	192	184
3	36	-51
4	133	125
5	122	-127
7	281	266
8	138	138
9	138	135
10	122	127
11	44	-55
13	84	81
14	91	95
15	38	45
17	24	18
18	28	-30
19	12	-14
20	9	-1
21	17	17
	4	0
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-24	35	30
-22	68	62
-20	114	-104
-18	150	145
-16	108	91
-12	233	218
-10	101	91
-8	275	-262
-6	143	135
-4	278	-301
-2	695	-793E
0	77	70
2	169	-161
4	353	-368
6	61	-57
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10	123	125
12	267	-256
14	203	187
16	152	128
18	58	-52
20	103	93
22	32	23
	4	1
-24	85	86
-23	69	66
-22	52	45
-21	47	-36
-20	59	-54
-18	205	202
-17	240	270
-16	62	-65
-15	88	-100
-14	107	-121
-12	160	150
-11	300	292
-10	370	-386
-9	181	-185
-8	179	-190
-7	111	-99
-6	20	-47
-5	150	142
-4	410	-401
-3	33	-17
-2	164	-154
-1	193	188
0	159	155
1	266	-254
2	58	60
3	120	114
4	223	-208
5	46	-32
6	476	481
7	237	-237
8	72	80
9	54	-50
10	180	-191
11	69	67
12	314	308
13	97	97
14	72	-70
17	58	45
18	15	24
19	57	46
20	24	-26
21	43	39
	4	2
-25	59	60
-22	13	-27
-21	10	-29
-20	32	30
-19	49	54
-18	64	-72
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-13	13	-28
-12	47	56
-11	277	275
-10	408	-412
-9	402	-394
-8	105	100
-7	77	63
-6	201	187
-5	406	398
-4	564	-525
-3	724	-695
-2	289	266
-1	262	254
0	70	75
1	262	238
2	82	-79
3	156	-140
4	167	161
5	285	275
6	49	52
7	53	52
8	58	-65
9	67	65
10	111	114
11	88	93
12	127	-122
13	50	49
14	113	-123
15	66	-78
16	55	58
18	38	-41
19	42	46
20	81	-82
21	101	-99
22	22	24
	4	3
-24	7	-18
-23	11	-25
-22	13	23
-21	66	-64
-20	90	-94
-19	97	108
-17	160	-173
-16	64	69
-15	68	-67
-14	16	-22
-13	145	143
-12	30	-29
-11	377	-359
-9	82	74
-8	178	174
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-1	70	75
0	54	-59
1	155	-157
2	74	76
3	91	89
4	40	44
5	81	87
6	11	-15
7	94	-94
9	92	79
10	7	14
11	57	61
13	13	-30
10 4		
-21	42	54
-19	69	-73
-18	12	-21
-17	80	-71
-16	46	-50
-15	114	113
-14	53	39
-13	131	-130
-12	43	-31
-11	64	-65
-10	22	-30
-9	125	133
-8	90	103
-7	123	-129
-6	58	-60
-4	25	32
-3	103	118
-2	62	70
-1	125	-132
0	53	-61
1	125	125
2	27	33
3	51	57
4	26	-24
5	74	-74
7	69	67
8	42	-49
9	64	77

11	48	-58
11 0		
-22	118	99
-20	63	55
-18	217	-200
-16	157	148
-12	222	-215
-10	45	33
-6	137	-120
-4	23	37
-2	54	48
0	127	-119
2	197	187
4	38	-35
6	43	-46
8	178	166
14	39	33
11 1		
-23	10	-8
-22	12	-9
-21	38	38
-20	52	-54
-19	25	-23
-18	54	-52
-17	35	-25
-16	73	71
-15	112	101
-14	148	-125
-13	87	-90
-11	16	-32
-10	114	113
-9	118	130
-8	118	-121
-7	213	-202
-6	30	41
-5	16	13
-4	85	75
-3	82	68
-2	60	-67
-1	88	-73
0	51	34
1	69	64
2	72	66
3	124	107
4	22	-28
5	16	-12
7	36	30
8	66	54
9	12	11
10	43	-36
12	40	-33
13	26	-14
11 2		
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-21	39	-40
-15	59	-65
-14	21	24
-12	40	56
-10	21	-39
-8	52	50
-7	59	-56
-6	62	72
-5	52	63
-4	52	62
-3	110	119
-2	103	-111
-1	182	-171
0	135	135
1	187	169
3	15	27
4	131	-129
5	109	-110
6	44	46
7	97	98
9	27	-26
10	43	-42
11	28	-30
12	15	-15
11 3		
-21	37	-49
-17	26	35
-15	77	-93
-14	64	77
-13	62	75
-11	105	104
-10	52	52
-9	82	-86
-8	57	63
-7	145	145
-6	57	-59
-5	72	70
-4	52	-61

-3	112	-107
-2	23	14
-1	96	99
0	37	-39
2	78	-74
3	65	-69
4	27	31
5	11	-10
9	68	-71
11 4		
-19	96	105
-18	15	27
-17	93	-104
-16	17	-34
-15	71	69
-14	13	19
-13	103	106
-12	35	37
-11	102	-105
-10	39	-56
-9	61	65
-7	31	39
-6	49	57
-5	89	-95
-4	35	-37
-3	27	-23
-2	35	-43
0	57	66
1	127	-132
2	29	-33
3	25	24
6	29	28
7	55	-67
9	42	45
12 0		
-22	57	-63
-20	95	90
-18	30	32
-16	120	-100
-14	149	132
-12	84	76
-10	166	-158
-8	200	187
-6	71	-66
-4	23	-21
-2	99	76
0	31	-36
4	54	52
8	68	-61
12 1		
-22	6	47
-21	34	-32
-20	57	52
-19	50	48
-18	48	-45
-17	93	-87
-16	55	48
-15	70	59
-14	51	49
-12	62	-55
-11	85	-79
-10	31	-31
-9	67	62
-8	78	77
-7	32	29
-6	88	-88
-5	124	-114
-4	81	-76
-3	22	23
-2	93	90
-1	81	79
0	144	-133
1	96	-87
2	22	-13
4	86	86
5	29	33
6	106	-99
7	12	-12
8	68	63
10	37	36
12 2		
-20	21	17
-19	47	52
-18	30	-37
-17	37	-50
-15	67	78
-13	19	31
-12	62	-62
-11	94	-95
-10	58	62
-9	121	124
-5	47	-49

-7	104	-115
-6	61	-61
-5	101	-113
-4	128	131
-3	73	78
-2	33	-35
-1	72	-69
1	72	-76
2	98	105
3	60	67
4	45	44
5	59	56
7	56	-59
8	45	51
9	51	57
11	31	34
12 3		
-20	15	-24
-19	55	-66
-17	32	41
-16	37	-38
-13	113	-122
-12	30	31
-11	57	-57
-8	47	57
-7	119	-125
-6	77	75
-4	57	-52
-3	79	80
-2	47	40
-1	81	-93
1	69	64
3	45	49
5	82	-89
6	32	-32
7	89	85
8	11	25
9	23	-22
12 4		
-19	9	17
-18	19	-24
-17	21	31
-16	46	55
-15	85	-94
-14	43	-49
-13	17	37
-12	13	23
-11	116	118
-10	87	94
-9	94	-98
-8	20	-23
-7	89	83
-5	38	43
-4	50	54
-2	14	-38
-1	54	52
8	21	25
9	21	-37
13 0		
-20	84	-85
-18	72	64
-16	81	-64
-14	94	-66
-12	52	46
-8	133	-110
-6	37	33
-4	64	58
-2	78	-70
0	108	94
2	34	35
6	64	55
8	29	-19
13 1		
-20	31	-29
-18	61	58
-16	74	-64
-15	54	-50
-12	149	131
-10	130	-119
-9	103	-92
-8	64	63
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-4	105	-98
-3	22	-24
-2	60	56
-1	42	37
0	15	36
1	49	50
2	28	-34
3	27	26
5	12	-28

6	42	40
7	41	36
8	54	-58
9	12	15
13 2		
-15	38	-38
-14	43	52
-13	37	46
-11	39	41
-10	19	-37
-9	39	-51
-8	36	39
-7	107	109
-6	65	-73
-5	13	16
-4	37	-42
-3	108	-118
-2	41	46
-1	134	132
0	57	-53
1	48	-49
2	62	-55
3	103	-107
4	76	76
5	96	101
6	51	-54
7	35	-35
9	13	-24
13 3		
-18	39	45
-17	57	-55
-15	68	76
-14	23	-26
-13	64	66
-12	50	46
-11	82	-84
-10	36	-45
-9	78	82
-8	49	-49
-7	36	39
-6	38	32
-5	106	-106
-4	48	-49
-3	47	55
-1	19	-29
1	47	-56
4	30	31
5	18	29
7	42	-53
13 4		
-17	7	81
-13	56	-59
-12	30	-32
-11	12	19
-10	24	-29
-9	12	13
-8	31	39
-7	28	-35
-6	31	-29
-5	31	-26
-4	25	-25
-3	28	33
-2	62	67
0	45	-43
4	24	28
6	27	-41
14 0		
-16	42	35
-12	87	-76
-10	66	52
-8	19	-21
-6	27	-33
-4	19	-17
0	43	-31
2	45	-32
4	57	55
6	38	-39
14 1		
-18	10	22
-17	40	38
-16	10	3
-15	30	-22
-14	64	-60
-13	12	18
-10	41	33
-9	40	-36
-8	76	-75
-6	33	-28
-5	58	-61
-4	88	79
-3	59	44

Table 1 (*cont.*)

-2	97	-92
-1	37	-32
0	18	22
2	78	68
3	59	52
4	49	-48
6	49	50
14 2		
-17	27	35
-16	40	-46
-14	15	-22
-13	88	-87
-12	40	39
-11	57	72
-10	45	-47
-9	58	-60
-7	52	-55
-6	70	75
-5	86	92
-4	50	-59
-3	36	-40

-2	17	21
-1	8	-22
0	51	50
1	78	78
2	35	-38
5	27	-34
8	21	29
14 3		
-16	9	20
-15	43	-53
-13	17	27
-11	32	35
-10	55	55
-9	62	-70
-7	46	53
-5	51	51
-4	28	26
-3	67	-71
-2	11	-24
-1	59	66
1	23	28

3	50	-62
14 4		
-13	32	38
-12	16	16
-11	34	-42
-10	30	-32
-9	35	39
-7	23	24
-4	15	-25
-2	9	-22
15 0		
-16	18	13
-6	97	85
-4	78	-79
-2	51	48
0	52	44
2	28	-28
15 1		
-16	32	38

-15	10	-4
-14	36	37
-13	10	3
-12	62	-65
-10	52	52
-9	22	23
-8	35	32
-6	66	-63
-5	10	-4
-4	27	29
0	33	-35
3	44	-49
15 2		
-15	35	46
-10	25	28
-9	40	44
-8	57	-59
-7	38	-40
-5	28	-38
-3	41	48
-2	45	-48

-1	43	-44
0	18	17
1	15	-20
2	33	42
15 3		
-13	45	-66
-12	40	-45
-11	30	39
-10	22	23
-9	30	-36
-7	54	-62
-5	9	23
-3	30	-22
0	17	19
15 4		
-7	22	-26
-5	42	57
16 0		
-12	44	44

-8	66	-63
-2	23	-29
16 1		
-10	32	-38
-9	17	19
-8	22	24
-7	38	-40
-6	30	31
-5	36	42
-4	34	-39
-3	22	-24
-2	37	40
16 2		
-7	26	36
-6	21	-29
-5	17	-26
-1	134	132
0	57	-53
1	48	-49

similar SFLS programs were used, one written by J. S. Rollett for the Mercury computer, and one by R. Diamand for Atlas. Both used a block diagonal approximation with allowance for interaction between the scale factor and overall temperature factor. The atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for carbon and nitrogen, that of Vaciago (1960) for sulphur, and that of Thomas & Umeda (1957) for zinc; those of zinc and sulphur were corrected for anomalous dispersion (Dauben & Templeton, 1955). The weighting scheme was such that $\sqrt{w}=F^*/|F_o|$ when $|F_o|>F^*$ and $\sqrt{w}=1$ otherwise, with $F^*=0{\cdot}28\,|F_o|_{\max}$. Throughout the refinement reflexions too weak to be observed were omitted. After successive cycles R fell to 0·17, 0·127, 0·123, 0·100, 0·086, 0·085, 0·085. After cycle 3 each layer was rescaled by comparison of the observed $|F_o|$ with $|F_c|$, the eight independent hydrogen atoms of pyridine and benzene were included in the structure factor calculation (but not refined), and the zinc and sulphur atoms were given anisotropic temperature factors. After cycle 4 all atoms except hydrogen and the methyl carbon atoms were allowed anisotropic vibrations. The standard deviations of parameters (e.s.d.) were estimated from the inverse of the last least-squares matrix. The parameter shifts in the last cycle were mostly well below 0·5 e.s.d.; the largest was 0·63 e.s.d.

Table 1 gives the observed and calculated structure factors, and Table 2 the final positional and thermal parameters. There is some evidence of extinction affecting the most intense reflexions; if those marked E in the list are omitted R becomes 0·081 for observed reflexions only, or 0·107 for all reflexions. Because of the limited data in the **b*** direction, the standard

Table 2. *Final positional parameters, with their estimated standard deviations* (× 10⁴) *and thermal parameters*

The B_{ij} values are in Å², comparable to the ordinary Debye factor; the atoms for which only one value is given have been treated as isotropic. Each hydrogen atom is bonded to the carbon atom with the same number.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Zn	0·6825 (1)	0·1693 (2)	0·1648 (1)	3·68	2·95	3·90	0·19	1·26	−0·10
S(1)	0·7827 (1)	0·1523 (3)	0·2950 (1)	4·59	5·06	3·54	0·50	0·81	−0·88
S(2)	0·7957 (1)	−0·0657 (3)	0·1788 (1)	4·75	3·95	4·14	−0·52	1·88	−0·21
S(3)	0·7235 (1)	0·4397 (3)	0·1361 (1)	6·20	3·28	3·97	0·19	0·33	−1·11
S(4)	0·6152 (1)	0·1943 (3)	0·0310 (1)	6·01	4·85	3·23	−0·50	1·28	−0·48
N(1)	0·5266 (3)	0·1304 (8)	0·1774 (2)	3·33	3·76	3·30	0·07	1·00	−0·19
N(2)	0·9151 (4)	−0·1120 (9)	0·3069 (3)	4·80	5·37	5·44	−0·21	1·40	−1·38
N(3)	0·6632 (4)	0·5086 (9)	0·0018 (3)	5·13	5·68	4·11	1·19	0·95	0·29
C(1)	0·4546 (5)	0·0382 (10)	0·1330 (3)	4·64	3·38	3·71	0·24	0·67	−0·55
C(2)	0·3491 (5)	0·0139 (11)	0·1378 (3)	4·49	5·37	5·73	1·55	0·43	−1·04
C(3)	0·3158 (5)	0·0919 (12)	0·1899 (4)	4·49	4·66	9·34	1·85	2·38	0·14
C(4)	0·3928 (6)	0·1905 (12)	0·2376 (4)	6·32	6·28	8·56	−0·76	3·90	0·57
C(5)	0·4960 (5)	0·2052 (11)	0·2291 (3)	4·94	5·66	4·87	−1·19	2·02	−0·29
C(6)	0·8397 (4)	−0·0162 (10)	0·2652 (3)	3·42	4·54	4·71	−0·57	2·02	−0·17
C(7)	0·9667 (7)	−0·2539 (14)	0·2813 (4)	6·77					
C(8)	0·9561 (7)	−0·0760 (14)	0·3816 (4)	7·34					
C(9)	0·6669 (4)	0·3916 (10)	0·0503 (3)	3·99	4·18	3·97	0·07	1·57	0·26
C(10)	0·6107 (6)	0·4734 (12)	−0·0712 (4)	5·96					
C(11)	0·7079 (7)	0·6777 (13)	0·0183 (4)	7·38					
C(12)	0·7052 (5)	−0·1189 (12)	0·0316 (4)	5·16	6·01	5·28	0·24	0·76	−0·55
C(13)	−0·0119 (6)	−0·0822 (12)	0·0570 (3)	5·63	6·85	4·64	0·69	1·43	−1·31
C(14)	−0·0876 (6)	0·0345 (12)	0·0262 (4)	5·47	6·68	5·61	−0·07	2·23	−0·74
H(1)	0·4799	−0·0226	0·0911	3·8					
H(2)	0·2905	−0·0634	0·1009	5·2					
H(3)	0·2331	0·0750	0·1960	5·8					
H(4)	0·3648	0·2513	0·2781	6·7					
H(5)	0·5543	0·2834	0·2661	5·1					
H(12)	0·1328	−0·2178	0·0582	5·4					
H(13)	−0·0232	−0·1491	0·1020	5·0					
H(14)	−0·1554	0·0580	0·0488	5·7					

Table 3. *Bond lengths and angles in the* PZDMC *molecule*

				e.s.d.
Zn —S(1)	2·598 Å	Zn —S(4)	2·612	0·004 Å
Zn —S(2)	2·330	Zn —S(3)	2·325	
Zn —N(1)	2·079			0·006
S(1) -C(6)	1·707	S(4) -C(9)	1·707	0·010
S(2) -C(6)	1·727	S(3) -C(9)	1·732	
C(6)-N(2)	1·333	C(9)-N(3)	1·342	0·013
N(1)-C(1)	1·320	N(1)-C(5)	1·342	
C(1)-C(2)	1·379	C(4)-C(5)	1·367	0·015
C(2)-C(3)	1·376	C(3)-C(4)	1·413	
N(2)-C(7)	1·466	N(3)-C(11)	1·465	0·017
N(2)-C(8)	1·484	N(3)-C(10)	1·473	

S(1) -Zn —N(1)	95·9°	S(4) —Zn —N(1)	93·9°
S(2) -Zn —N(1)	116·1	S(3) —Zn —N(1)	116·8
S(1) -Zn —S(2)	73·4	S(4) —Zn —S(3)	72·9
S(1) -Zn —S(3)	102·6	S(4) —Zn —S(2)	102·1
S(1) -Zn —S(4)	170·2	S(2) —Zn —S(3)	127·1
Zn —N(1)-C(1)	121·0	Zn —N(1)-C(5)	120·7
N(1)-C(1)-C(2)	124·3	N(1)—C(5)-C(4)	122·5
C(1)-C(2)-C(3)	117·3	C(3)—C(4)-C(5)	118·3
C(2)-C(3)-C(4)	119·3	C(1)—N(1)-C(5)	118·3
Zn —S(1) -C(6)	79·9	Zn —S(4) -C(9)	80·4
Zn —S(2) -C(6)	87·9	Zn —S(3) -C(9)	88·9
S(1) -C(6)-S(2)	118·3	S(4) —C(9)-S(3)	117·3
S(1) -C(6)-N(2)	120·5	S(4) —C(9)-N(3)	123·3
S(2) -C(6)-N(2)	121·2	S(3) —C(9)-N(3)	119·4
C(6)-N(2)-C(7)	122·1	C(9)—N(3)-C(11)	123·9
C(6)-N(2)-C(8)	124·0	C(9)—N(3)-C(10)	119·5
C(7)-N(2)-C(8)	114·0	C(10)-N(3)-C(11)	116·5

The e.s.d. is 0·3° for angles around the zinc atom, rising to 1·5° for angles involving carbon and nitrogen atoms only.

deviations of *y* coordinates are higher than the others, and because of the method of layer scaling used vibration parameters in the **b*** direction have little meaning.

Description and discussion

The molecule of $\mathrm{PZD_MC}$ is illustrated in Figs. 1 and 2, and Table 3 gives bond lengths and angles. The coordination group around zinc is a distorted trigonal bipyramid, with coplanar atoms Zn, N(1), S(2), and S(3) lying in the equatorial plane, and S(1) and S(4) occupying the axial positions. The axial Zn–S bonds (average 2·60 Å) are significantly longer than the equatorial bonds (average 2·33 Å). The main departures from trigonal symmetry are the difference in the length of the equatorial Zn–N(1) and Zn–S bonds, the angle S(2)–Zn–S(3), which is 127° instead of 120°, and the deviation of the axial Zn–S bonds by 17° from the normal to the equatorial plane; exact trigonal symmetry would not, of course, be possible for a compound with this chemical structure.

Gillespie (1963) states that in trigonal bipyramidal complexes of the type MX_5 the axial bonds should be slightly longer than the equatorial ones as a result of electron pair repulsions, but in $\mathrm{PZD_MC}$ the observed differences are larger than any that Gillespie mentions. A 'normal' Zn–S bond length is ~2·4 Å – the sum of the covalent radii is 2·35 (Pauling, 1960); in bis(dimethyldithiocarbamato)zinc ($\mathrm{ZD_MC}$) (Klug, 1966) zinc is bound to four sulphur atoms at distances between 2·31 and 2·44 Å, making a distorted tetrahedron. In bis(diethyldithiocarbamato)zinc ($\mathrm{ZD_EC}$) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965) there are four sulphur atoms at distances between 2·33 and 2·44 Å from zinc, but also one at 2·82 Å. The axial bonds in $\mathrm{PZD_MC}$ are therefore longer than normal, and this may be attributed to the amine coordination, or the increase in coordination number to five, or to both.

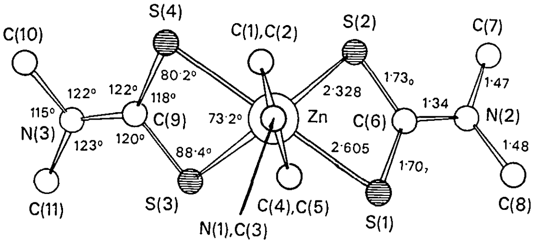

Fig. 1. One molecule of $\mathrm{PZD_MC}$ viewed along the molecular twofold axis. The bond lengths and angles in the two dithiocarbamate groups have been averaged.

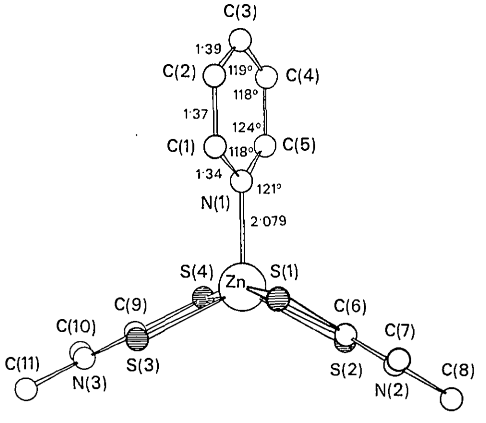

Fig. 2. One molecule of $\mathrm{PZD_MC}$ projected onto the equatorial plane N(1)S(3)S(2) of the distorted trigonal bipyramid. The planar dithiocarbamate groups are very nearly perpendicular to this plane.

The molecule of $\mathrm{PZD_MC}$ has approximately twofold symmetry. The twofold axis of pyridine, through N(1) and C(3), nearly coincides with that of the rest of the molecule; the angle between them is 4°, the pyridine being tilted in a direction approximately normal to its own plane so that its approach to S(4), 3·48 Å, is closer than to S(1), 3·55 Å. This distortion appears to be caused by a larger number of intermolecular contacts on one side of the pyridine ring than on the other.

The two dimethyldithiocarbamate groups are planar (apart from the methyl hydrogen atoms) within experimental error (Table 4). Their planes are approximately normal to the equatorial plane of the trigonal bipyramid (Fig. 2). Zinc is 0·086 Å from the plane of one group and 0·037 Å from the plane of the other; these are significant displacements and are in the opposite senses relative to the approximate molecular twofold axis. The slight shortening of S(1)–C(6) and S(4)–C(9) relative to the other two S–C bonds is possibly significant, and could be associated with the lengthening of the bonds from these sulphur atoms to zinc. In other respects the dimensions of the dimethyldithiocarbamate group are not significantly different from those in $\mathrm{ZD_MC}$ itself (Klug, 1966) or those found in the dithiocarbamates of nickel (II), copper (II), and zinc (II) (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965; Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965; Bonamico, Mazzone *et al.*, 1965).

The bond lengths and the angles in the benzene and pyridine rings are all within two e.s.d.'s of the values in the parent compounds (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958), except for N(1)–C(1) and N(1)–C(5). These are shorter than the corresponding bonds in pyridine but comparable to those found in dipyridinecobalt dichloride and dipyridinecopper dichloride (Dunitz, 1957).

Fig. 3 shows the arrangement of molecules in the crystal lattice. Neighbouring pyridine rings are packed with their planes approximately normal to each other, in a herringbone pattern, extending along **b**. The molecules are held together by van der Waals forces only; there are nine intermolecular contacts shorter than 3·80 Å and the shortest of these is 3·68 Å [S(4).....C(1)]. There is a large cylindrical space parallel to **b** between benzene molecules; only C(8) appears to prevent the benzene molecules from moving along these channels, and escaping from the crystal. The benzene molecules also act as 'buffers' between sheets of $\mathrm{PZD_MC}$ molecules normal to [100], which have no mutal contacts less than 3·90 Å.

In Fig. 4 the molecule of PZD$_{\mathrm{M}}$C, as found from this accurate analysis, is compared with the *b*-axis electron density projection of crystals of form A. The stereochemistry is the same in the two forms except for the orientation of the pyridine ring. This ring is probably fairly free to rotate about the Zn–N(1) bond direction, avoiding the region where it is eclipsed with S(1) and S(4), but otherwise adopting the orientation which packs most satisfactorily in the crystal lattice.

Our sincere thanks are due to Dr B. Saville of the Natural Rubber Producers Research Association who suggested the study of this problem and supplied many crystals. We thank Dr J.S. Rollett, Dr R. Diamand and Dr L. Hodgson for the use of computer programs, and the Edinburgh University Computer Unit, the Manchester University Computing Laboratory, and the Atlas Computer Laboratory of the Science Research Council (Chilton, Berks.) for their cooperation. A D.S.I.R. Research Studentship to K.A.F. is gratefully acknowledged.

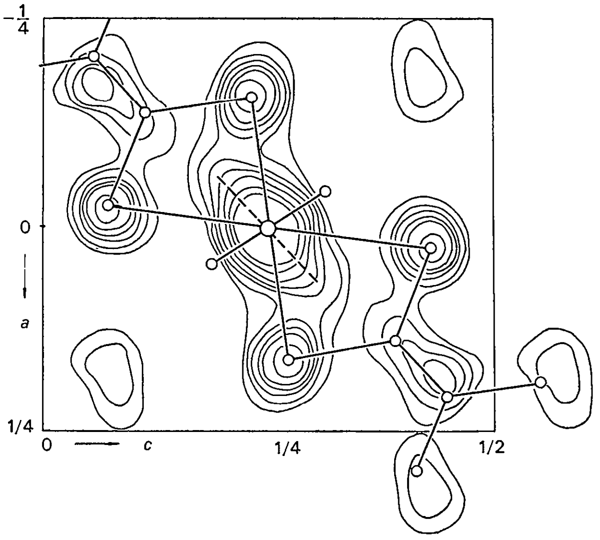

Fig. 4. *b*-Axis electron density projection for crystal of form A. The molecule shown in full lines is that found from the analysis of crystals of form B, in projection along its two-fold axis. The dotted line shows the orientation of the pyridine ring suggested in form A.

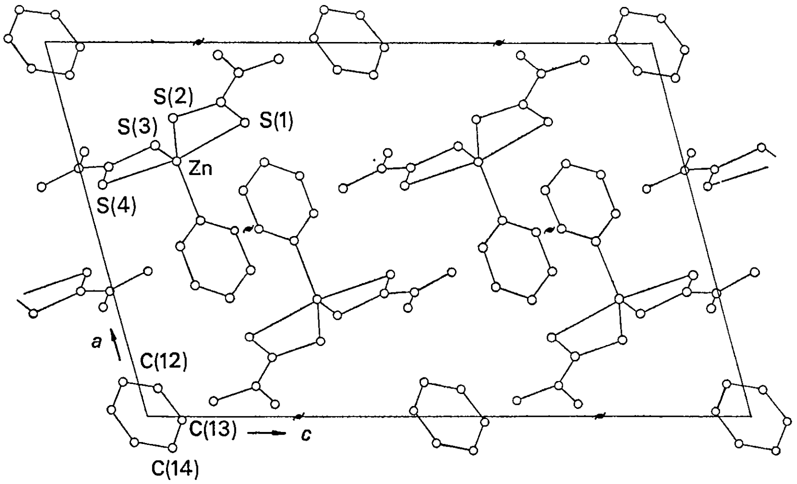

Fig. 3. *b*-Axis projection showing the packing of molecules in form B.

Table 4. *Planarity of various groups of atoms*

The equation of each best plane is $Ax+By+Cz+D=0$

A	*B*	*C*	*D*	Atoms included in best plane calculation Displacement from plane (Å)						Displacement of other atoms	
Pyridine											
1·815	−6·405	10·45	−1·975	N(1) −0·002	C(1) −0·005	C(2) 0·009	C(3) −0·006	C(4) 0·000	C(5) 0·004	Zn	−0·099
Dithiocarbamate group											
9·945	4·723	−7·657	−6·238	S(1) −0·005	S(2) 0·005	C(6) −0·005	N(2) 0·016	C(7) −0·023	C(8) 0·010	Zn	−0·086
Dithiocarbamate group											
11·99	−2·450	−6·815	−6·668	S(4) 0·007	S(3) −0·011	C(9) 0·012	N(3) 0·011	C(11) 0·022	C(10) −0·035	Zn	−0·037
Equatorial plane											
1·184	1·720	18·38	−4·121	Zn 0·009	S(2) −0·005	S(3) −0·005	N(1) −0·012			S(1) S(4)	2·49 −2·49
Benzene											
5·019	5·648	9·231	0	C(12) 0·003	C(13) −0·003	C(14) 0·003	C(12′) −0·003	C(13′) 0·003	C(14′) −0·003		

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An X-ray Study of the Effect of Manganese on the Occurrence of Stacking Faults in Silver-Base Alloys

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(*Received* 5 *April* 1966)

X-ray diffraction line profiles from filings of silver–manganese alloys in the solid-solution range were recorded by a Geiger counter X-ray diffractometer. Stacking-fault parameters α and β were obtained from peak position and peak asymmetry measurements and the concentration of deformation faults has been found to be negligibly small. The broadening of the powder-pattern peaks was studied by Fourier analysis of line shapes and the anisotropic values of the effective particle sizes $[D_e]_{hkl}$ and the root-mean-square strains $[\langle\varepsilon_L^2\rangle]^{1/2}_{hkl}$ were obtained in all cases. Appreciable change in $[D_e]_{hkl}$ was not observed across the solid-solution range and the measured effective particle sizes are primarily a consequence of deformation and twin faulting. A good agreement was observed for the compound fault probability $(1{\cdot}5\alpha+\beta)$ obtained by two different methods.

Introduction

During recent years a great deal of attention has been given to the X-ray diffraction study of cold-worked metals and alloys as it is able to reveal a fairly detailed picture of the deformed state. It has been observed that cold working produces appreciable changes in the intensity distribution of diffracted X-rays and it is well established that the broadening of X-ray powder diffraction line profiles of f.c.c. metals and alloys results from a reduction in the size of the coherently diffracting domains, from distortion within these coherent domains and from stacking faults on (111) planes. Besides peak broadening, peak shift and peak asymmetry are also observed and are chiefly due to deformation and twin stacking faults (Warren, 1959).

Since stacking faults exert an important influence on the structural and mechanical properties of f.c.c. metals and alloys, extensive measurements on the occurrence of stacking faults in binary alloys based on the solvent metals copper and silver have been performed (Warren & Warekois, 1955; Wagner, 1957; Davies & Cahn 1962; Adler & Wagner, 1962; Foley, Cahn & Raynor, 1963; Vassamillet & Massalski, 1964; Sen Gupta & Quader, 1966; Goswami, Sen Gupta & Quader, 1966*a*). All these investigations have shown pronounced increase of the faulting probability with increasing solute content and the dependence of stacking fault parameter α on solute concentration is either linear or roughly parabolic. Recently, to observe the effects of the transition metals manganese and nickel on the occurrence of stacking faults in copper-base alloys, measurements have been carried out by Henderson (1963–64), Nakajima & Numakura (1965) and Goswami, Sen Gupta & Quader (1966*b*) and a quite different and interesting picture has been obtained in these systems. The concentration of stacking faults has been found to be small and the variation of the fault parameter α with increasing solute content is neither linear nor parabolic.

In view of this, the present investigation, which is concerned with the observation of the effect of transition solute manganese on the occurrence of stacking faults in silver-base alloys, has been taken into consideration and Warren & Averbach's method (Warren, 1959) of Fourier analysis of line shapes has been