Table 2. *The crystal and molecular parameters of the two refined poly-L-proline II models*

The angles in italics were not refined.

	Non-statistical	Statistical
τ_{23}	*−23·8°*	*−23·8°*
τ_{34}	*31·4*	*31·4*
τ_{45}	*94·7*	*94·7*
τ_{56}	95·1	96·5
τ_{67}	180·4	176·5
τ_{78}	200·2	201·8
θ_x	1·0	−1·8
θ_y	232·4	231·2
θ_z	55·2	54·5
D	1·244 Å	1·243 Å
ψ	42·4°	10·7°
ROT	–	−65°
TRANS	–	−6·923 Å
K	2·400	2·413
B	5·10 Å²	0·832 Å²

The refined crystal structure we prefer is very similar to that of Burge *et al.* (1962), and has standard (*J. Mol. Biol.* (1966), **15**, 399) polypeptide chain parameters $\varphi=99\cdot8°$, $\psi=-95\cdot1°$, $\omega=-0\cdot4°$.

Table 3. *The cylindrical polar coordinates of the basic (up) poly-L-proline chain unit*

	Non-statistical			Statistical		
	R (Å)	φ (°)	Z (Å)	R (Å)	φ (°)	Z (Å)
αC(3)	1·24	0	0	1·24	0	0
C(1)	0·27	12·0	1·16	0·32	14·7	1·20
N(1)	1·04	−75·3	1·95	1·03	−73·9	1·97
O(1)	1·14	114·6	1·34	1·15	109·2	1·41
αC(1)	1·24	−120·0	3·10	1·24	−120·0	3·10
βC(1)	2·64	−105·2	3·40	2·65	−106·1	3·35
γC(1)	3·19	−79·2	2·86	3·21	−80·2	2·82
δC(1)	2·45	−67·3	1·66	2·44	−67·4	1·65

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The crystal structure of Zr₂Se*

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The crystal structure of Zr₂Se has been determined and refined by X-ray single-crystal methods. Zr₂Se was found to be isostructural with Ta₂P [Nylund, *Acta Chem. Scand.* (1966), **20**, 2393] and with Ti₂S [Owens, Conard & Franzen, *Acta Cryst.* (1967), **23**, 77].

The coordination polyhedra types between trigonal prismatic and tetrakaidecahedral found for boron, silicon and phosphorus in many compounds of these elements with transition elements (Aronsson, Lundström & Rundqvist, 1965) were recently found also for sulphur in Ti₂S (Owens, Conard & Franzen, 1967) and in Nb₂₁S₈ (Franzen, Beineke & Conard, 1968). The work reported here was carried out with the purpose of further exploring the crystal chemistry of the lower chalcogenides of transition elements, and in particular to determine whether other cases of augmented trigonal prismatic coordination could be found for chalcogens.

The method of high temperature preparation has been described previously (Owens, Conard & Franzen, 1967). In the case of Zr₂Se the sample was prepared at a final annealing temperature of 1550°C. The single-crystal X-ray diffraction data were collected with a Hilger–Watts full circle diffractometer coupled to an SDS-910 computer in

a configuration described elsewhere (Dahm, Benson, Nimrod, Fitzwater & Jacobsen, 1967). Mo $K\alpha$ radiation was used with balanced Zr and Y filters to collect data for about 1300 reflections at $2\theta \le 80°$.

The Lorentz, polarization and absorption corrections were applied as described previously (Franzen, Beineke & Conard, 1968). The standard deviations of all observations were obtained with the use of the law of propagation of errors and estimated standard deviations in the θ angle and the absorption factor and standard deviations in the intensities (corrected for background) based on counter statistics. Data were accepted only if $\sigma(I)/I < 0\cdot4$, leaving 438 independent reflections.

The lattice parameters were determined from a Guinier powder photograph at 25°C using KCl as internal standard and Cu $K\alpha_1$ radiation, $\lambda = 1\cdot54050$ Å:

$$a = 12\cdot6400 \pm 27 \text{ Å}, \ b = 15\cdot7968 \pm 32 \text{ Å}, \ c = 3\cdot6016 \pm 10 \text{ Å},$$
$$V = 719\cdot1 \pm 3 \text{ Å}^3.$$

With $Z = 12$, (*cf.* below), $D_x = 7\cdot24$ g.cm⁻³.

By comparison of the Weissenberg pattern of Zr₂Se with that of Ti₂S it seemed likely that these two compounds are isostructural. Accordingly the Ti₂S positions were used as

a starting model for the structure of Zr_2Se, and this model was refined by full-matrix least-squares calculation with the computer program *ORFLS* (Busing, Martin & Levy, 1962). The atomic scattering factors used were those given by Hanson, Herman, Lea & Skillman (1964). The real part of the anomalous dispersion correction as given in *International Tables for X-ray Crystallography* (1962) was applied to the scattering factor for zirconium. In Ti_2S there are twelve formula units in nine fourfold positions in the mirror planes of the space group *Pnnm* (No. 58). In addition to the eighteen corresponding positional parameters, nine independent isotropic temperature factor coefficients and one scale factor were refined. The overdetermination of the structure was thus greater than fifteen-fold.

The weights, w, were taken to be reciprocals of the squares of the standard deviations, obtained as discussed above. The quantity minimized in the least-squares procedure was $\Sigma w(|F_{obs}| - |F_{calc}|)^2$. An unweighted R value of 0·106 was obtained after several cycles, and further cycles of calculation did not result in further refinement of the structure; all parameter shifts were < 1% of the e.s.d.'s of the parameters. The value obtained for the quantity commonly

Table 1. *Least-squares refined parameters of the crystal structure of Zr_2Se*

All atoms are in the point position $4(g)$ $x,y,0$ of the space group *Pnnm*.

	$10^4X/a$	$10^4Y/b$	B
Zr(1)	1522±5	242±4	0·52±12 Å²
Zr(2)	775±5	2534±5	0·64±11
Zr(3)	5829±5	801±4	0·20±10
Zr(4)	4681±5	3912±4	0·35±11
Zr(5)	7988±5	2028±4	0·18±12
Zr(6)	8767±5	4221±4	0·23±11
Se(1)	4206±5	2083±4	0·22±11
Se(2)	2447±5	4191±4	0·38±12
Se(3)	6806±5	3476±4	0·13±11

Table 2. *Interatomic distances in Zr_2Se (± 0·01 Å)*

Reference atom	Coordinated atom	Number of coordinated atoms	Distance
Se(1)	Zr(2)	2	2·75 Å
	Zr(5)	2	2·75
	Zr(6)	2	2·79
	Zr(3)	1	2·88
	Zr(4)	1	2·95
Se(2)	Zr(5)	2	2·72
	Zr(3)	2	2·73
	Zr(1)	2	2·77
	Zr(4)	1	2·86
	Zr(6)	1	2·94
Se(3)	Zr(5)	1	2·73
	Zr(6)	1	2·74
	Zr(1)	2	2·74
	Zr(2)	2	2·74
	Zr(4)	1	2·78

Table 3. *Observed and calculated structure factors for Zr Se*

```
H  F(O)  F(C)    11 204 -200    1  65   55    K=14,L= 0    10  93  -57    K= 4,L= 1    K= 9,L= 1    16  99 -117    5  96   71    1 246  254
               12  96   81    2 355 -327    0 166  144                1 261  269    0 122  102                             3 111 -101
K= 0,L= 0      13 200  219    3  82   58    1 117  -85    K=24,L= 0    2 408 -463    1 130 -120    K=15,L= 1    K= 0,L= 2    4  92   92
2  27  -22     14 212  224    4 114  114    2 159 -139    0 119  124    3  79  -71    2 165 -157    0 140  128    4  97 -110    5 181 -182
4 151 -147     20  83   57    5  85   67    5 208  207    5 130 -116    5  88  103    3 243 -241    3 179  168    6 132 -136    7  62  -24
6 165 -170     21 114 -111    7  71   69    6 107  -98    6 157 -190    6  49  -33    4 106  -94    6  79  -52    8  94 -116    8 226 -244
8 135 -137                    8  66  -43    7 170 -166                7  61  -44    5 129  126    7 111   80   12 116  123   10 125 -126
12 113  142    K= 5,L= 0     10  74   47   11 113 -127    K=25,L= 0    8  63   66    9  96   87    8 168 -161                11  77   69
18 198 -231    2  69  -57    11 126 -126   13  81   71    1 112  -96    9 146 -141   11  76  -59    9 139 -126    K= 1,L= 2
               3 350 -345    13 112  -88   16 116  124    5 116  125   10  89   99   15 159 -140   11 100  117    3  56  -38    K= 8,L= 2
K= 1,L= 0      4 212 -206    14 111   95                             11  82   67   16  97   89   18  93  -85    5 206  243    0  91  -85
2  26    4     9  86   92    17  87  -69    K=15,L= 0    K=27,L= 0    12  94  -64                             6  71   46    1 235 -230
3  54  -52    12 116  132                   1 141 -126    3 103   72   16 119 -142                K=16,L= 1    7  90  109    2 123  123
5 268  310    14 174 -154    K=10,L= 0      4 102   97    4  94  -30   17  85 -101    K=10,L= 1    1  98   93    9 111 -143    3  93   99
6  57   58    15  90   93    0 168  155     5 121   90                22  99   99    1 184 -156    6 228  226   10 133  151    6  78  101
7 131  134    16  91  -92    1 120 -110     6  97  -86    K= 0,L= 1                 2 101  104    7 145 -128                7 130 -150
9 159 -169    18  98   75    4 102   91     8 147 -123    1  54  -71    K= 5,L= 1    4 156  153                K= 2,L= 2    8  80  -57
10 172  177                   5  87  -73                  3 235 -282    0 443  465    5 253  237    K=17,L= 1    3  73  -59
12  70   49    K= 6,L= 0     6  82  -68    K=16,L= 0     7 113  120    1 188 -198    9  68   39    0 145 -142    5 239  280    K= 9,L= 2
17  83  -74    0 351 -327    7 103   84    0 126 -116    9 117  135    2 104  -93   13 131 -147    2 110 -104    6 100   88    2 285 -269
               1  58   22   11 224  238    2  89   76   11 163 -189    3  53   58   16  98   83    3 118  110    8 186  244    4  88   98
K= 2,L= 0      2 195 -176   15 110 -116    3 227 -200                4  63   53   18  93   70    8  94  115   10 152 -171    7  76   59
0  27  -28     3 276 -254   19  98   86    5 115   90    K= 1,L= 1    7  70  -73                11 146  134                11 102 -114
2  63  -61     6 343  381                   6  88  -81    0  79  -80    8  70   67    K=11,L= 1   14 113 -133    K= 3,L= 2
3  82  -77     8 117 -128    K=11,L= 0      7  95  -75    1  75   72    9  74   66    1 115  -93   16 118  118    4 103  119    K=10,L= 2
4  62  -53     9 154 -155    1  63  -50     9 106 -106    2  53   53   11 174  179    3 261 -248                5 175 -193    0 143  131
5 294  357    11  87   89   18 114  115                  3 185 -209   12  80  -87    5 136  116    K=18,L= 1    6  63  -67    1  86  -92
6 109  114   18 114  115    2 203  194    K=17,L= 0     4 159 -173   13  77  -83    7 105  -87    1 125 -128    8 111  130    4  87   76
8 269  291   22  93   41    3 127  104    3 179  156    5 225 -264                8 154 -154    2 189 -176   10 137  166    7  93   74
9  79   61                   4 174  138    4 178 -166    7  98  101    K= 6,L= 1               3  87   65   13 163  190    9  85   39
10 159 -159    K= 7,L= 0    6 331  314    5 172 -168    8 149 -155    2  59   40    K=12,L= 1    4  88   74
14  81  -77    1 352  318    8 184 -168   12 112 -147    9  79  -82    3 118  121    1 121   98    K=19,L= 1    K= 4,L= 2    K=11,L= 2
               3 135 -124   10 155 -182   16 110  -64   10  62   52    4 137  147    2  94  -99    6 149 -144    3  70   56    2 174  158
K= 3,L= 0      4 125  115   12 107  108                11 186  182    6 205  202    3  93   89    7  97 -105    4 125 -121    4 115  115
2  45  -36     5 222 -221   19  82   46    K=18,L= 0    15  99 -117    8 107 -117    5 175 -170   16 114  112    5 220  247    5  69   38
4 165  159     8 283 -286                  0 264 -251   16 120 -133                6  77  -64                7  60  -43    6 267  273
5 228 -240    10 149 -145    K=12,L= 0     2  94   99                 K= 7,L= 1    8 146 -160    K=20,L= 1    8  73  -70    8 130 -146
6  85  -79    11 102   77    0 148  146    4 114  115    K= 2,L= 1    0 128 -126                2  81   68    9  83  -74
7  83   75   13 139  125    6 150 -149    6  97  122    3 128 -138    1  67   66    K=20,L= 1    3  85   75   11 153 -177    K=12,L= 2
8 144  151   16  98   93    7 132  122    9  95 -113    4 232 -257    2  59  -67    2  59   92    7 136 -149                0 132  124
10 178  188   19 141 -166    8 118  107   -12  93  -98    5  44  -41    3  54  -31   20  92   41    8  86  -88    K= 5,L= 2    4  73  -57
12  74   51                  11 165  165   13 109  100    6 118  129    5 204  211                             3 263 -268    6 136 -128
13 175  207    K= 8,L= 0    12 105  116   14 116  -78    7 207  219    7 100   97    K=13,L= 1    K=21,L= 1    4 152 -163    7 100  108
14  83 -101    0 124  -58   14  81  -58                  8 102  -96    8 340  353    0 215 -200    1 153 -130    9  73   80    8 119   96
16  73  -61    1 306 -283   15 114 -104    K=19,L= 0    10 146 -154   10 219 -217    1 153 -130    2 243  240   12 102  118
17  72  -45    2 165  153                  1 103  123   11  87  -78   11  93   70    2 243  240    4  77   46                K=13,L= 2
19 116 -134    3  99  116    K=13,L= 0     4  96   72                              4  77   46    7  96  -90    K= 6,L= 2    1 168 -163
               6 131  116    1 200 -189                 K= 3,L= 1    K= 8,L= 1    7  96  -90   16 164 -157    0 267 -251    2 180 -179
K= 4,L= 0      7 167 -174    2 237 -208    K=20,L= 0    0  95   96    1  66   51                             2 156 -136    8  90  109
0  39  -27     8  86  -68    5 108   80    7  90   85    3 385  453    5 222 -213    K=14,L= 1    2 156 -136    3 203 -204
1  55   34   10  67  -78    8 119  119    8 155 -189    4  50  -53    7 117 -114    2 147 -136    K=22,L= 1    6 286  316    K=14,L= 2
3  71   72   11  76   52   10 135  147                  6 196  206    8  80   64    9 104  -98    2 124  117    7  67   21    0 143  130
4 153 -158   13 108 -115   16  89  -86    K=22,L= 0    7 164 -176    9 104  -98   11 120  130    3  86   85    8 112 -113    2  95 -121
5 228  309   16  89  -86   19 100  111    0 224 -238    9 279 -293   11 120  130   12 141  151                9 117 -133    5 199  183
6  65  -73                              12  91   87   10 106 -122   12 141  151   13 240  236    K=23,L= 1   11  82   79    6  86  -88
8  84  -85                16 114 -134    K=23,L= 0   14  83  -92   13 240  236                2 101   97
9  96  -86    K= 9,L= 0                  1 107 -120                11 170 -185    K=23,L= 1    K= 7,L= 2
                                                                    13 188 -199    2 101   97
```

referred to as the standard deviation of an observation of unit weight, $[\Sigma w \Delta^2/m - n]^{\frac{1}{2}}$ (m is the number of observations, n is the number of variables), was 1·25. The parameters obtained are presented in Table 1. The Se–Zr interatomic distances implied by these parameters are presented in Table 2. The data of Table 1 demonstrate that Zr_2Se is isostructural with Ta_2P (Nylund, 1966) and with Ti_2S. The setting used by Nylund differs from that used here by an interchange of the a and b axes. The fact that Ta_2P, Ti_2S and Zr_2Se are isostructural is not an unexpected result considering their similar radius ratios and valence electron configurations. It has further been shown by the data of Table 2 that selenium, as well as sulphur, exhibits coordination as high as seven and eight fold with augmented trigonal prismatic arrangement of the metal atoms. A list of F_{obs} and F_{calc} is given in Table 3.

A view of the bonding of chalcogens in trigonal prismatic (Franzen, 1966), and augmented trigonal prismatic (Owens, Conard & Franzen, 1967; Franzen, Beineke & Conard, 1968) environments has been presented which attributes the occurrence of these coordination configurations to the involvement of the chalcogen d orbitals in the chemical bonding. It would seem that this view of the bonding is unavoidable in the case of Zr_2Se, since the $4d$ levels of both Zr and Se are of nearly the same energy, and thus they surely will mix in the formation of a valence band in Zr_2Se. The metal coordination in compounds of this structure type has recently been discussed (Franzen, Smeggil & Conard, 1967).

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The cell constants and space group of the complex $(C_6H_5)_3Sn.Mn(CO)_5$ By KH. A. I. F. M. MANNAN, *Physics Department, Dacca University, Dacca-2, East Pakistan.*

The cell constants for the complex $(C_6H_5)_3Sn.Mn(CO)_5$ are $a = 15·91 \pm 0·01$, $b = 16·32 \pm 0·01$, $c = 32·12 \pm 0·02$ Å; $\beta = 95·0 \pm 0·1°$. There are two molecules in each asymmetric unit. The crystal belongs to the space group $C2/c$.

The complex $(C_6H_5)_3Sn.Mn(CO)_5$ would be expected to have a direct metal to metal bonding as the crystals are diamagnetic. As a part of a study of metal to metal bonds between such dissimilar metal atoms, the crystal structure determination of this complex by X-ray diffraction methods was undertaken.

The crystals are monoclinic. The cell constants determined from zero-layer Weissenberg photographs about a and b axes with Cu $K\alpha$ radiation are:

$$a = 15·91 \pm 0·01, \; b = 16·32 \pm 0·01, \; c = 32·12 \pm 0·02 \text{ Å};$$
$$\beta = 95·0 \pm 0·1°.$$

The density observed by the method of flotation was 1·74 g.cm^{-3}, and the calculated density for 16 molecules in the unit cell was 1·74 g.cm^{-3}.

The systematic absences observed from Weissenberg photographs for the 0 to 4th layers about the a axis, the 0 to 9th layers about the b axis, and the 0 and 1st layers about the c axis may be summarized as below:

Reflexions hkl are present for $h + k = 2n$.
Reflexions $h0l$ are present for $l = 2n$, and $h = 2n$.
Reflexions $0k0$ are present for $k = 2n$.

Thus, from all these conditions of systematic absences, the space group is either no. 9, Cc or no. 15, $C2/c$ (*International Tables for X-ray Crystallography*, 1952).

A three-dimensional Patterson synthesis revealed linear concentrations at $0, y, \frac{1}{4}$ and planar concentrations at $x, 0, z$. This shows that the space group is $C2/c$ (Buerger, 1959). This creates the problem of placing two molecules in each asymmetric unit.

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