Acta Cryst. (1963). **16**, 843

The crystal structures of selenium dicyanide and sulphur dicyanide.

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(*Received* 26 *February* 1963)

The crystal structure of selenium dicyanide, $Se(CN)_2$, has been determined by two-dimensional X-ray analysis; the analogous sulphur dicyanide, $S(CN)_2$, has been shown to be isomorphous with the selenium compound.

Both compounds crystallize in the orthorhombic system, with space group *Cmca* (D_{2h}^{18}), and with the following unit-cell dimensions:

	a (Å)	*b* (Å)	*c* (Å)
$Se(CN)_2$	$8{\cdot}71 \pm 0{\cdot}02$	$6{\cdot}98 \pm 0{\cdot}02$	$13{\cdot}41 \pm 0{\cdot}05$
$S(CN)_2$	$8{\cdot}60 \pm 0{\cdot}02$	$6{\cdot}85 \pm 0{\cdot}05$	$12{\cdot}80 \pm 0{\cdot}10$

The measured density for $Se(CN)_2$, 2·17 g.cm^{-3}, indicates that there are 8 molecules in the unit cell, so that the molecules must lie in special positions. The crystals are tabular on (001), bounded by {110}, and cleave very readily perpendicular to {001}; the crystals tend to grow slightly bent, which resulted in rather poor photographs. Comparison of the cell dimensions, space groups and observed intensities showed the two compounds to be isomorphous.

Fehér, Hirschfeld & Linke (1963) report $S(CN)_2$ as being orthorhombic, with $a = 10{\cdot}80$, $b = 12{\cdot}70$, $c = 5{\cdot}31$ Å, with space group $P2_12_12_1$ (D_2^4), and with 4 molecules in the unit cell; their axes correspond approximately to $d(110)$ and $\frac{1}{2}d(1\bar{1}0)$, but the angle $110 : 1\bar{1}0$ is 77°. It is possible that sulphur dicyanide is polymorphic, but even so the cell parameters of Fehér *et al.* appear to be incorrect since their unit cell containing 4 molecules of $S(CN)_2$ has a larger volume (728 Å^3) than that of $S_3(CN)_2$ ($V = 549$ Å^3, Fehér *et al.*; $V = 564$ Å^3, Foss, 1956) which also contains 4 molecules.

Selenium dicyanide was chosen for the structure determination as it gave better photographs than the sulphur compound. The selenium atoms were located from Patterson projections down the three principal axes, the carbon and nitrogen atoms from difference syntheses. The atomic co-ordinates and isotropic thermal parameters were refined by the method of least squares to a discrepancy index of $R = 0{\cdot}12$ (a comparison of observed and calculated structure factors is given in Table 1). The final atomic coordinates (in fractions of cell edges) and mean-square amplitudes of vibration (in Å^2) are given in Table 2.

The *V*-shaped molecules lie in planes perpendicular to the *c* axis (Fig. 1); hence the ease of cleavage. The

Table 1. *Observed and calculated structure factors*

l	$\lvert F_o \rvert$	F_c
	0 0 1	
4	299	-336
8	165	162
10	9	12
12	61	-70
14	12	-8
16	27	27
	0 2 1	
0	104	-106
1	83	-68
3	90	-77
4	76	85
5	54	57
7	63	69
8	50	-51
9	36	-39
11	36	-44
12	24	25
13	20	20
15	16	22
16	6	-10
	0 4 1	
0	83	-86
1	61	67
3	62	65
4	74	73
5	44	-49
7	41	-47
8	44	-46
9	27	27
11	24	28
12	20	24
13	9	-12
15	14	-13

l	$\lvert F_o \rvert$	F_c
	0 6 1	
0	60	61
4	54	-54
8	30	38
12	20	-21
	0 8 1	
1	25	-22
3	24	-22
5	18	17
7	15	17
	2 0 1	
4	135	-119
8	100	90
12	46	-50
	4 0 1	
4	121	-132
8	81	85
12	37	-44
	6 0 1	
4	112	-103
8	63	65
12	35	-33
	8 0 1	
4	59	-44
8	33	31
12	13	-18

l	$\lvert F_o \rvert$	F_c
	10 0 1	
4	53	-28
k	$\lvert F_o \rvert$	F_c
	2 k 0	
0	135	127
2	87	-70
4	79	-76
6	65	62
	4 k 0	
0	150	154
2	81	-57
4	63	-59
6	69	46
	6 k 0	
0	143	122
2	61	-41
4	36	-39
6	30	33
	8 k 0	
0	57	49
2	37	-19
4	37	-24
	10 k 0	
0	46	31

Table 2. *Atomic parameters*

	x/a	*y/b*	*z/c*	$\bar{u}^2$
Se	0·00	0·16	0·122	0·05
C	0·18	0·29	0·125	0·10
N	0·32	0·41	0·125	0·14

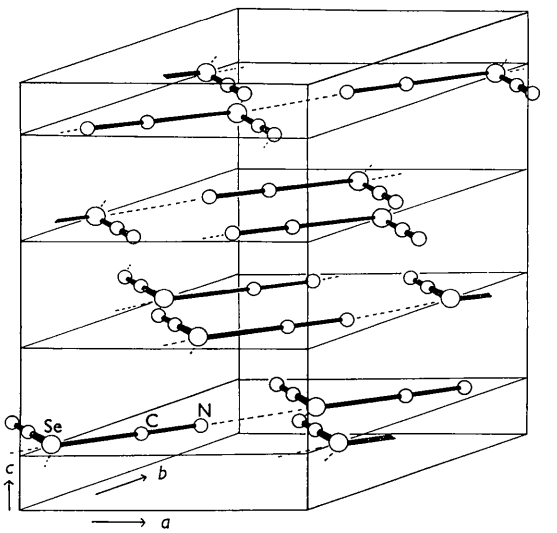

Fig. 1. A clinographic drawing of a unit-cell and contents.

molecules necessarily possess the symmetry $m = C_s$. The bond lengths and angles, together with their estimated standard deviations, are given in Table 3. The accuracy

Table 3. *Bond lengths and angles*

Se–C	1·86 Å	with $\sigma = 0{\cdot}10$ Å
C–N	1·42 Å	with $\sigma = 0{\cdot}15$ Å
Se–C–N	177°	with $\sigma = 6°$
C–Se–C	119°	with $\sigma = 6°$

of these values is so low that no conclusions about the nature of the bonding can be drawn. The closest approach between neighbouring molecules is between selenium and nitrogen atoms (close approaches shown by dotted lines in Fig. 1); the distance between these is 2·35 Å, with standard deviation 0·10 Å, which is significantly shorter than the sum of the van der Waals radii (3·5 Å).

The calculations were carried out on the Durham University Pegasus Computer with programs devised by Cruickshank & Pilling (1961) and Samet. The atomic scattering factors used were those of Thomas & Umeda (1957) for selenium, and Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and nitrogen.

The author is indebted to Mr M. J. Sprague for providing the compounds, and to British Titan Products Ltd for a Research Fellowship.

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Acta Cryst. (1963). **16**, 844

Electron-diffraction evidence of an outward growth tendency in electrolytic crystal growth.

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(*Received* 30 *January* 1963 *and in revised form* 25 *February* 1963)

The present authors have systematically studied, by electron diffraction, the structure and growth of iron electrodeposits on copper (100), (110) and (111) single-crystal substrates. The work has been described in detail elsewhere (Reddy, 1958; Reddy & Wilman, 1959). The purpose of this short communication is to describe an interesting observation made on iron electrodeposits on the copper (110) face.

Results

The epitaxy of iron on the copper (110) face corresponded to Fe (211) || Cu (110) with Fe [$\bar{1}$11] || Cu [1$\bar{1}$0]. This orientation relationship only stipulates that two crystal axes of iron are fixed relative to the copper substrate lattice. The third axis can take up one of two possible positions. Thus the iron deposit crystals can grow on the copper (110) face in two crystallographically equivalent ways without violating the requirements of epitaxy. Corresponding to each of these orientations there is a particular electron diffraction pattern. With the electron beam along the Cu [1$\bar{1}$0] azimuth the hexagonal patterns from the two possible orientations coincide with each other. When, however, the beam is along the Cu [001] azimuth, each orientation contributes a distinct rectangular spot pattern (the sides of the rectangle being in the ratio 1:$\sqrt{2}$) with the 211 spot in the plane of incidence (Figs. 1 and 4).

The interesting feature of patterns with the beam

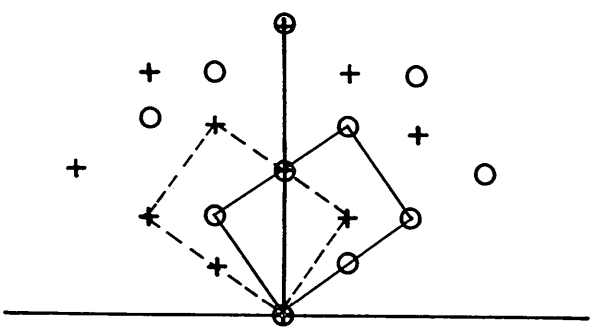

Fig. 4. Theoretical pattern based on Fe (211) || Cu (110) and Fe [$\bar{1}$11] || Cu [1$\bar{1}$0] with beam parallel to Cu [001] azimuth.

along the Cu [001] azimuth concerns the *intensity* of the component $\sqrt{2}$-rectangle patterns. Figs. 1, 2 and 3, for example, are patterns obtained from 1000 Å thick iron deposits from a ferrous ammonium sulphate (350 g.l^{-1}) — sulphuric acid (2·5 g.l^{-1}) bath with a current density of 25 mA.cm^{-2} at room temperature (20 °C). They show that the two component patterns are equal in intensity only in Fig. 1, which has been taken with the electron beam grazing the flat middle part of the single-crystal surface. At the curved edges of the specimen, where the surface deviates slightly from the Cu (110) plane, Figs. 2 and 3 show that one of the component patterns is much more intense than the other. That component pattern is more intense in which the line joining the 000 and 011 spots makes a smaller angle

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