

The Crystal Structure of Selenium Bis(diethyl-dithiocarbamate)

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The structure of selenium bis(diethylthiocarbamate), $\text{Se}[\text{Et}_2\text{NCS}_2]_2$, has been determined by means of three-dimensional X-ray methods. The yellow crystals are orthorhombic with $a=9.711 \pm 0.005$ Å, $b=25.533 \pm 0.010$ Å, $c=6.655 \pm 0.005$ Å, $Z=4$ and space group $D_2^4-P2_12_12_1$. The density of the crystals is calc. 1.52, found 1.50 g/cm³.

Using $\text{CuK}\alpha$ radiation and multiple-film Weissenberg techniques, 1236 intensities were estimated visually. The structure was refined by full-matrix least squares methods to a conventional R value of 6.2 %.

The molecules are monomeric, each selenium atom being bonded to all four sulphur atoms of the two ligands in the molecule, forming an asymmetric, planar complex. Some relevant bond lengths and angles are, $\text{Se}-\text{S}_1=2.312 \pm 0.005$ Å, $\text{Se}-\text{S}_2=2.719 \pm 0.005$ Å, $\text{Se}-\text{S}_3=2.332 \pm 0.004$ Å, $\text{Se}-\text{S}_4=2.779 \pm 0.005$ Å, $\angle \text{S}_1-\text{Se}-\text{S}_2=70.9 \pm 0.2^\circ$, $\angle \text{S}_1-\text{Se}-\text{S}_3=87.7 \pm 0.2^\circ$, $\angle \text{S}_3-\text{Se}-\text{S}_4=70.9 \pm 0.2^\circ$ and $\angle \text{S}_2-\text{Se}-\text{S}_4=131.5 \pm 0.2^\circ$. The C_1-N_1 and C_2-N_2 bond lengths are 1.33 and 1.38 Å, respectively, indicating considerable double bond character for these bonds in accord with transfer of charge from nitrogen to sulphur atoms.

One of the four ethyl groups in a molecule seems to be oriented in two different ways, the result being a disordered structure with a statistical distribution of orientations.

The present structure investigation is part of the study undertaken in this laboratory of compounds of divalent tellurium and selenium with dithio and related anions.¹⁻⁸ The compounds whose structures have been determined so far,^{3,5-8} all demonstrate the tendency of divalent tellurium and selenium to form planar four-coordinate structures. Only two of those structures, *viz.*, those of tellurium di(ethylxanthate)⁵ and tellurium di(morpholydithiocarbamate)⁸ are four-coordinate complexes based on intramolecular bonds only. In the other structures, two weak intermolecular bonds complete the four-coordination. In the xanthate and dithiocarbamate, the average length of each of the two three-center systems $\text{S}-\text{Te}-\text{S}$ consisting of two $\text{Te}-\text{S}$ bonds *trans* (150°) to each other, was found to be 5.36 Å. Exactly the same length

has been found in centro-symmetrical *trans* tellurium complexes with thiourea or substituted thioureas as sulphur-containing ligands.⁹

For selenium, the data available from Se—Se—Se linear three-center systems found in triselenocyanate ions,⁹⁻¹² indicate a central selenium atom radius of 1.49 Å. It was expected that the structure of selenium bis(diethyl-dithiocarbamate) would be related to those of the analogous tellurium compounds,^{5,8} and it would therefore be of interest to see if the length of the S—Se—S three-center system was close to that predicted (5.06 Å) from the selenium radius of 1.49 Å.

EXPERIMENTAL

The preparation of selenium bis(diethyl-dithiocarbamate),^{13,14} $\text{Se}[\text{Et}_2\text{NCS}_2]_2$, and its use in connection with analytical methods¹⁵ have been reported. Crystals used in the present investigation were made by the procedure used to prepare divalent selenium bis(dialkyl-dithiophosphates) and bis(dialkyl-dithiophosphinates).¹ Russel also obtained selenium bis(diethyl-dithiocarbamate) by a similar method.¹³ An aqueous solution of sodium diethyl-dithiocarbamate was added, with stirring, to selenious acid dissolved in 2 N hydrochloric acid, in the molar ratio 4:1. The resulting yellow oil was dissolved in warm benzene and cooled. The yellow crystals which formed, were dissolved in boiling alcohol. Upon cooling, yellow prisms crystallized out (m.p. 105°C).

The orthorhombic crystals are elongated along *c*. Unit cell data were computed from 62 high-order reflections, read from NaCl-calibrated Weissenberg *0kl* and *hk0* films, using a least squares program "CELLDIM". This program plus the other programs used in the computations were made available by the Weizmann Institute of Science, Rehovoth, Israel. They were modified for use on the IBM 360-50H computer at the University of Bergen, by Dr. Dove Rabinovich. The cell dimensions are, $a = 9.711 \pm 0.005$ Å, $b = 25.533 \pm 0.010$ Å and $c = 6.655 \pm 0.005$ Å. There are four molecules per unit cell with density, calc. 1.52, found 1.50 g/cm³. From systematic extinctions, *h*00, 0*k*0, and 00*l* for *h*, *k*, and *l* odd, the space group is $D_2^4 - P2_12_12_1$.

Integrated Weissenberg equi-inclination photographs were taken of the *0kl*, *1kl*, *hk0*, *hkl*, *hk2*, and *hk3* layers, using the multiple-film technique and Ni-filtered CuK radiation. Reflection intensities were estimated visually and 1236 out of 1471 independent reflections with $\sin \theta \leq 0.985$ were observed and measured. (The reflection 020 was caught by the beam stop). The crystals used for the *a* and *c* axis photographs had cross-sections of 0.10×0.13 and 0.07×0.09 mm², respectively. Usual Lorentz and polarization corrections were applied, but the intensities were not corrected for absorption ($\mu = 78$ cm⁻¹).

STRUCTURE SOLVING

Patterson projections were computed along the *a* and *c* axes. From these, the *x* and *y* coordinates for the selenium and sulphur atoms were found; however, their *z* coordinates were difficult to ascertain. Fourier refinements and use of molecular models based upon assumed bond lengths and angles, enabled us to arrive at the proper solution. Further Fourier refinements gave all atomic positions except for the two carbon atoms of one of the four ethyl groups. The position of this group could therefore only be tentatively fixed.

At this stage of refinement, all reflections were brought to the same scale by comparison of reflections common to two layers. The structure was then further refined by means of full-matrix, least squares methods. The least squares program employed ("BDLS") minimizes the expression $\sum w[|F_o| - |kF_c|]^2 / \sum wF_o^2$, where *k* is a variable scale factor in the computation, and *w*, the relative weight assigned to a reflection, is equal to $1/\sigma^2(F)$. $\sigma^2(F)$ is evaluated

as $(ka_1)^2 + (a_2F_o)^2/4w_o$, where w_o is a weight factor related to the reliability with which the intensity of a given reflections is measured, and a_1 and a_2 are constants, here put equal to 2.0 and 1.0, respectively.

After a few cycles of refinement with isotropic temperature factors, the reliability index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ had decreased to 0.085. Nevertheless, the bond lengths, angles and temperature parameters of the C₄-C₅ ethyl group were obviously in error. A three-dimensional Fourier synthesis, based on reflections with signs determined from a structure factor calculation excluding C₄ and C₅ was then computed for the part of space where C₄ and C₅ could possibly be located. Four peaks corresponding to ca. 1.5 - 2 e/Å³ each were found, three of them overlapping. Putting C₄ and C₅ in positions corresponding to the two highest peaks gave reasonable bond lengths and angles. All reflections were then given a common scale factor after being rescaled by comparison between observed and calculated structure factors.

Anisotropic temperature factors were introduced for the heavy atoms; however, by further refinement C₄ and C₅ ended up much as before. Difference maps were then computed for the *a* and *c* axes projections, excluding C₄ and C₅ from the corresponding structure factor calculations. Four peaks corresponding to 2 e/Å² each were found in the *hk0* map, and a wide electron density maximum corresponding to 3.1 e/Å² was found in the suspect ethyl group region in the *0kl* map. Use of the molecular model, the three-dimensional Fourier and the two-dimensional difference Fourier maps finally gave as a result that there are two types of molecules, due to two different configurations of the C₄-C₅ ethyl group, statistically distributed in the crystals. The two ethyl group configurations are related by rotation around the N₁-C₄ bond; however, due to interatomic repulsions not only the C₅ but also the C₄ atom occupy different positions in the two configurations. These are called A and B, respectively, and A and B have been added as indices to the two atoms. Based on a statistical (1:1) distribution of the two types of molecules the structure refined satisfactorily, the *R*-value converging to 0.062. A final three-dimensional difference synthesis of the section of space around the above ethyl group showed no maxima or minima larger than 0.4 e/Å³.

Final observed and calculated structure factors are listed in Table 1. Atomic scattering factors for selenium, sulphur, nitrogen, and carbon listed in *International Tables*¹⁶ were used. The atomic scattering factors for selenium and sulphur were corrected for anomalous dispersion according to Cromer,¹⁷ using *f'* and *f''* values from the *International Tables*.¹⁶ Final positional parameters are listed in Table 2, while the components of atomic vibration tensors are listed in Table 3. Interatomic distances and angles based on coordinates from Table 2 are listed in Tables 4 - 6.

THE STRUCTURE OF THE SELENIUM BIS(DIETHYLDITHIOCARBAMATE) MOLECULE

One molecule of selenium bis(diethyldithiocarbamate), Se[Et₂NCS₂]₂, represents an asymmetric unit. In Fig. 1 the molecules are viewed along the *a* axis, and in Fig. 2 along the *c* axis. In the latter figure, some intermolecular distances are indicated to illustrate the packing of the molecules in the crystals.

Table 1. Observed and calculated $0kl$, $1kl$, $hk0$, $hk1$, $hk2$ and $hk3$ structure factors ($\times 10$). Negative F_o values indicate that the corresponding reflection is unobserved.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	4	0	1022	1330	0	20	3	-81	38	0	11	7	213	218	1	14	3	335	337
0	6	0	410	471	0	21	3	-43	0	0	12	7	63	119	1	15	3	-65	63
0	8	0	133	117	0	22	3	133	133	0	13	7	61	66	1	16	3	371	397
0	10	0	96	19	0	23	3	-78	12	0	14	7	-58	11	1	17	3	136	113
0	12	0	295	251	0	24	3	149	143	0	15	7	147	160	1	18	3	280	280
0	14	0	464	466	0	25	3	-73	69	0	16	7	-50	43	1	19	3	155	155
0	16	0	305	287	0	26	3	-68	67	0	17	7	-45	45	1	20	3	136	133
0	18	0	940	877	0	27	3	133	126	0	0	8	105	124	1	21	3	165	161
0	20	0	-77	61	0	28	3	167	170	0	1	8	116	107	1	22	3	169	167
0	22	0	426	388	0	29	3	-50	4	0	2	8	-54	37	1	23	3	260	258
0	24	0	-81	7	0	30	3	87	99	0	3	8	-54	71	1	24	3	-65	39
0	26	0	212	220	0	0	4	377	313	0	4	8	91	100	1	25	3	126	116
0	28	0	100	100	0	1	4	541	566	0	5	8	-52	25	1	26	3	119	120
0	30	0	103	92	0	2	4	-64	47	0	6	8	83	93	1	27	3	115	119
0	32	0	60	79	0	3	4	712	675	0	7	8	-48	20	1	28	3	65	75
0	1	1	1140	1242	0	4	4	-65	21	0	8	8	102	131	1	29	3	78	77
0	2	1	1319	1376	0	5	4	650	575	0	9	8	-43	16	1	30	3	84	107
0	3	1	956	954	0	6	4	541	566	0	10	8	129	129	1	0	4	381	354
0	4	1	91	79	0	7	4	432	408	0	11	8	155	203	1	1	4	361	354
0	5	1	574	488	0	8	4	364	345	1	1	1	527	531	1	2	4	151	131
0	6	1	156	131	0	9	4	661	632	1	2	1	425	412	1	3	4	783	326
0	7	1	85	63	0	10	4	307	299	1	3	1	1105	1122	1	4	4	372	353
0	8	1	457	445	0	11	4	286	279	1	4	1	1279	1308	1	5	4	343	331
0	9	1	184	197	0	12	4	178	180	1	5	1	1222	1239	1	6	4	336	348
0	10	1	299	293	0	13	4	182	202	1	6	1	257	199	1	7	4	389	405
0	11	1	295	364	0	14	4	206	189	1	7	1	588	611	1	8	4	322	326
0	12	1	464	450	0	15	4	358	340	1	8	1	368	335	1	9	4	193	191
0	13	1	262	263	0	16	4	-40	35	1	9	1	681	666	1	10	4	530	519
0	14	1	150	150	0	17	4	170	186	1	10	1	200	198	1	11	4	252	277
0	15	1	813	791	0	18	4	128	134	1	11	1	124	125	1	12	4	215	247
0	16	1	272	270	0	19	4	99	90	1	12	1	183	187	1	13	4	-67	47
0	17	1	-70	20	0	20	4	-79	7	1	13	1	753	746	1	14	4	175	166
0	18	1	266	263	0	21	4	172	174	1	14	1	561	586	1	15	4	355	359
0	19	1	643	608	0	22	4	-75	64	1	15	1	220	176	1	16	4	121	135
0	20	1	-78	11	0	23	4	129	120	1	16	1	153	160	1	17	4	215	247
0	21	1	356	348	0	24	4	-68	55	1	17	1	467	432	1	18	4	-70	71
0	22	1	-90	32	0	25	4	141	129	1	18	1	352	329	1	19	4	187	198
0	23	1	304	298	0	26	4	-58	56	1	19	1	269	264	1	20	4	-69	79
0	24	1	-81	5	0	27	4	92	76	1	20	1	251	235	1	21	4	158	153
0	25	1	247	235	0	28	4	-43	11	1	21	1	278	287	1	22	4	16	16
0	26	1	-77	40	0	1	5	425	391	1	22	1	193	196	1	23	4	195	191
0	27	1	118	102	0	2	5	536	504	1	23	1	93	86	1	24	4	-59	37
0	28	1	-69	43	0	3	5	564	544	1	24	1	130	115	1	25	4	94	93
0	29	1	113	98	0	4	5	-76	22	1	25	1	176	184	1	26	4	-50	11
0	30	1	-58	1	0	5	5	200	287	1	26	1	81	77	1	27	4	93	111
0	31	1	61	71	0	6	5	401	403	1	27	1	140	142	1	28	4	-104	103
0	0	2	981	781	0	7	5	-78	17	1	28	1	-60	59	1	0	5	358	328
0	1	2	203	189	0	8	5	-78	16	1	29	1	95	101	1	1	5	240	212
0	2	2	98	89	0	9	5	79	95	1	30	1	-49	48	1	2	5	154	130
0	3	2	169	155	0	10	5	259	242	1	31	1	119	132	1	3	5	334	338
0	4	2	-44	58	0	11	5	345	341	1	32	1	37	47	1	4	5	606	611
0	5	2	78	74	0	12	5	197	175	1	0	2	105	43	1	5	5	66	83
0	6	2	437	411	0	13	5	221	198	1	1	2	50	31	1	6	5	125	159
0	7	2	60	62	0	14	5	107	117	1	2	2	596	525	1	7	5	214	198
0	8	2	661	581	0	15	5	-91	43	1	3	2	610	578	1	8	5	503	484
0	9	2	1066	1069	0	16	5	243	265	1	4	2	555	532	1	9	5	97	103
0	10	2	356	330	0	17	5	166	163	1	5	2	238	210	1	10	5	120	139
0	11	2	-58	76	0	18	5	86	93	1	6	2	731	755	1	11	5	225	236
0	12	2	661	644	0	19	5	-75	36	1	7	2	674	677	1	12	5	155	152
0	13	2	927	891	0	20	5	204	196	1	8	2	616	586	1	13	5	46	76
0	14	2	277	295	0	21	5	176	203	1	9	2	-46	12	1	14	5	171	183
0	15	2	226	213	0	22	5	-64	52	1	10	2	614	634	1	15	5	107	247
0	16	2	519	507	0	23	5	-60	2	1	11	2	711	703	1	16	5	109	121
0	17	2	390	372	0	24	5	199	207	1	12	2	368	346	1	17	5	68	72
0	18	2	311	288	0	0	6	198	177	1	13	2	195	182	1	18	5	214	224
0	19	2	184	187	0	1	6	191	194	1	14	2	541	528	1	19	5	129	141
0	20	2	293	273	0	2	6	114	111	1	15	2	537	542	1	20	5	-62	59
0	21	2	224	226	0	3	6	94	124	1	16	2	293	274	1	21	5	-84	35
0	22	2	190	155	0	4	6	81	43	1	17	2	277	258	1	22	5	188	213
0	23	2	-91	17	0	5	6	-81	66	1	18	2	311	315	1	23	5	63	78
0	24	2	-74	65	0	6	6	-81	19	1	19	2	275	273	1	24	5	40	40
0	25	2	-77	84	0	7	6	-81	25	1	20	2	215	228	1	25	5	-70	81
0	26	2	231	218	0	8	6	89	72	1	21	2	241	247	1	26	5	76	93
0	27	2	193	190	0	9	6	180	171	1	22	2	234	222	1	0	6	-70	84
0	28	2	-65	34	0	10	6	88	84	1	23	2	99	101	1	1	6	99	80
0	29	2	-59	39	0	11	6	215	204	1	24	2	162	153	1	2	6	141	138
0	30	2	128	126	0	12	6	160	152	1	25	2	143	140	1	3	6	188	194
0	31	2	152	176	0	13	6	135	131	1	26	2	213	227	1	4	6	-70	46
0	1	3	283	289	0	14	6	-75	73	1	27	2	-60	66	1	5	6	99	102
0	2	3	-53	55	0	15	6	-73	57	1	28	2	105	120	1	6	6	141	131
0	3	3	392	284	0	16	6	113	129	1	29	2	120	134	1	7	6	222	236
0	4	3	94	73	0	17	6	185	195	1	30	2	77	94	1	8	6	92	106
0	5	3	423	376	0	18	6	130	148	1	31	2	73	70	1	9	6	-68	50
0	6	3	515	521	0	19	6	-60	32	1	0	3	60	61	1	10	6	69	93
0	7	3	700	659	0	20	6	-56	29	1	1	3	555	519	1	11	6	227	229
0	8	3	600	59															

Table 1. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
3	4	0	381	328	6	19	0	-90	26	11	11	0	59	60	5	1	1	447	440	8	22	1	81	80
3	5	0	288	334	6	20	0	-89	23	11	12	0	55	51	5	2	1	882	871	8	23	1	85	106
3	6	0	195	64	6	21	0	-86	3	11	13	0	196	188	5	3	1	263	261	8	24	1	52	59
3	7	0	421	410	6	22	0	163	150	12	4	0	65	85	5	4	1	-63	18	9	0	1	-85	49
3	8	0	493	455	6	23	0	-40	42	12	0	0	-53	38	5	5	1	574	605	9	1	1	266	270
3	9	0	851	888	6	24	0	-75	7	12	1	0	-53	41	5	6	1	571	572	9	2	1	295	287
3	10	0	435	418	6	25	0	-70	12	12	2	0	-52	12	5	7	1	499	499	9	3	1	216	199
3	11	0	272	254	6	26	0	101	103	12	3	0	125	138	5	8	1	189	212	9	4	1	94	83
3	12	0	335	304	7	1	0	116	85	12	4	0	79	77	5	9	1	259	281	9	5	1	204	203
3	13	0	1004	1067	7	2	0	593	584	12	5	0	-48	23	5	10	1	196	198	9	6	1	226	223
3	14	0	334	319	7	3	0	289	286	12	6	0	0	41	5	11	1	578	571	9	7	1	111	110
3	15	0	228	239	7	4	0	-93	72	12	7	0	151	158	5	12	1	260	264	9	8	1	118	120
3	16	0	-80	27	7	5	0	111	105	2	0	1	369	348	5	13	1	312	326	9	9	1	164	159
3	17	0	512	496	7	6	0	711	681	2	1	1	507	444	5	14	1	187	163	9	10	1	164	155
3	18	0	298	296	7	7	0	165	132	2	2	1	416	429	5	15	1	321	342	9	11	1	90	93
3	19	0	-88	30	7	8	0	211	189	2	3	1	324	265	5	16	1	322	313	9	12	1	-79	81
3	20	0	296	303	7	9	0	87	89	2	4	1	175	219	5	17	1	212	217	9	13	1	86	91
3	21	0	359	353	7	10	0	275	265	2	5	1	486	455	5	18	1	159	148	9	14	1	-75	64
3	22	0	-57	7	7	11	0	126	122	2	6	1	197	201	5	19	1	120	122	9	15	1	73	76
3	23	0	30	68	7	12	0	440	426	2	7	1	1012	1045	5	20	1	277	293	9	16	1	112	116
3	24	0	109	97	7	13	0	189	179	2	8	1	1205	1230	5	21	1	156	168	9	17	1	119	125
3	25	0	231	239	7	14	0	-91	26	2	9	1	510	511	5	22	1	152	158	4	18	1	62	66
3	26	0	93	95	7	15	0	157	144	2	10	1	372	407	5	23	1	112	123	9	19	1	71	70
3	27	0	221	241	7	16	0	228	243	2	11	1	909	878	5	24	1	209	223	9	20	1	105	112
3	28	0	-71	4	7	17	0	-719	498	2	12	1	727	707	5	25	1	-71	37	9	21	1	57	54
3	29	0	-66	38	7	18	0	-88	7	2	13	1	191	172	5	26	1	191	123	9	22	1	63	63
3	30	0	-58	11	7	19	0	105	88	2	14	1	439	410	5	27	1	-60	28	10	1	1	207	195
3	31	0	122	222	7	20	0	102	91	2	15	1	252	257	5	28	1	107	117	10	1	1	113	90
4	0	0	449	446	7	21	0	-78	24	2	16	1	304	300	5	29	1	-58	78	10	2	1	97	101
4	1	0	392	409	7	22	0	-75	10	2	17	1	75	75	6	0	1	59	10	10	3	1	89	80
4	2	0	250	261	7	23	0	-70	37	2	18	1	262	232	6	1	1	201	216	10	4	1	226	222
4	3	0	853	858	7	24	0	130	149	2	19	1	170	170	6	2	1	450	467	10	5	1	51	51
4	4	0	161	195	8	0	0	683	663	2	20	1	317	308	6	3	1	308	328	10	6	1	122	120
4	5	0	301	308	8	1	0	360	344	2	21	1	103	106	6	4	1	286	282	10	7	1	101	102
4	6	0	37	43	8	2	0	-88	0	2	22	1	210	208	6	5	1	316	319	10	8	1	152	149
4	7	0	619	621	8	3	0	118	126	2	23	1	98	98	6	6	1	398	412	10	9	1	82	86
4	8	0	410	357	8	4	0	507	489	2	24	1	229	242	6	7	1	570	570	10	10	1	88	103
4	9	0	94	71	8	5	0	180	171	2	25	1	136	134	6	8	1	340	350	10	11	1	78	84
4	10	0	308	258	8	6	0	-90	53	2	26	1	200	210	6	9	1	392	402	10	12	1	127	116
4	11	0	320	304	8	7	0	158	137	2	27	1	92	99	6	10	1	145	143	10	13	1	92	94
4	12	0	76	65	8	8	0	206	192	2	28	1	98	116	6	11	1	490	478	10	14	1	107	107
4	13	0	142	139	8	9	0	91	50	2	29	1	85	90	6	12	1	198	197	10	15	1	-58	50
4	14	0	-79	42	8	10	0	-91	5	2	30	1	99	105	6	13	1	174	159	10	16	1	87	91
4	15	0	707	674	8	11	0	128	130	2	31	1	-48	30	6	14	1	293	255	10	17	1	66	71
4	16	0	-84	31	8	12	0	101	75	2	32	1	162	153	6	15	1	391	404	10	18	1	75	73
4	17	0	122	113	8	13	0	167	177	3	1	1	371	355	6	16	1	95	101	11	0	1	89	105
4	18	0	-88	34	8	14	0	165	189	3	2	1	102	112	6	17	1	-85	15	11	1	1	64	75
4	19	0	604	580	8	15	0	-88	24	3	3	1	535	521	6	18	1	201	200	11	2	1	148	158
4	20	0	187	167	8	16	0	-86	23	3	4	1	220	188	6	19	1	207	222	11	3	1	-67	36
4	21	0	206	215	8	17	0	185	155	3	5	1	785	932	6	20	1	116	125	11	4	1	81	77
4	22	0	172	165	8	18	0	197	219	3	6	1	1016	1057	6	21	1	-80	46	11	5	1	-65	37
4	23	0	165	175	8	19	0	-77	13	3	7	1	421	425	6	22	1	163	167	11	6	1	156	151
4	24	0	-87	22	8	20	0	73	61	3	8	1	948	904	6	23	1	97	104	11	7	1	-62	42
4	25	0	199	214	8	21	0	-69	9	3	9	1	302	261	6	24	1	139	145	11	8	1	80	82
4	26	0	148	135	8	22	0	220	217	3	10	1	567	552	6	25	1	90	110	11	9	1	-58	28
4	27	0	74	45	9	1	0	128	111	3	11	1	461	425	6	26	1	100	112	11	10	1	124	124
4	28	0	-67	11	9	2	0	399	366	3	12	1	663	657	6	27	1	61	79	11	11	1	70	65
4	29	0	120	112	9	3	0	-91	17	3	13	1	538	525	6	28	1	58	54	11	12	1	110	108
5	1	0	744	742	9	4	0	262	224	3	14	1	189	201	7	0	1	588	604	11	13	1	85	51
5	2	0	467	458	9	5	0	296	264	3	15	1	474	432	7	1	1	124	95	11	14	1	68	70
5	3	0	356	355	9	6	0	110	91	3	16	1	344	328	7	2	1	124	98	12	0	1	82	85
5	4	0	147	147	9	7	0	310	287	3	17	1	191	182	7	3	1	237	234	12	1	1	66	70
5	5	0	58	58	9	8	0	155	156	3	18	1	178	187	7	4	1	526	490	12	2	1	-86	32
5	6	0	69	107	9	9	0	156	137	3	19	1	267	275	7	5	1	319	325	12	3	1	-45	48
5	7	0	70	48	9	10	0	88	80	3	20	1	244	256	7	6	1	-80	84	12	4	1	89	104
5	8	0	-72	28	9	11	0	87	42	3	21	1	-85	23	7	7	1	190	175	12	5	1	96	105
5	9	0	407	467	9	12	0	113	93	3	22	1	259	250	7	8	1	255	257	2	0	2	617	611
5	10	0	395	394	9	13	0	188	137	3	23	1	111	104	7	9	1	594	584	2	1	2	947	1006
5	11	0	103	101	9	14	0	100	73	3	24	1	219	216	7	10	1	93	123	2	2	2	772	9

Table 1. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
3	9	2	365	346	6	10	2	205	186	10	1	2	196	202	3	26	3	58	82	7	3	3	331	325
3	10	2	274	272	6	11	2	149	165	10	2	2	170	179	3	27	3	68	81	7	4	3	259	248
3	11	2	243	239	6	12	2	283	276	10	3	2	234	228	3	28	3	71	82	7	5	3	213	206
3	12	2	127	121	6	13	2	165	156	10	4	2	61	62	3	29	3	48	57	7	6	3	144	133
3	13	2	309	293	6	14	2	249	272	10	5	2	113	120	4	0	3	289	277	7	7	3	-59	34
3	14	2	232	224	6	15	2	176	178	10	6	2	266	257	4	1	3	435	461	7	8	3	94	96
3	15	2	195	196	6	16	2	214	212	10	7	2	190	191	4	2	3	190	192	7	9	3	73	94
3	16	2	169	162	6	17	2	93	111	10	8	2	71	71	4	3	3	348	356	7	10	3	-59	44
3	17	2	245	279	6	18	2	171	160	10	9	2	69	75	4	4	3	252	246	7	11	3	103	92
3	18	2	322	306	6	19	2	134	143	10	10	2	117	128	4	5	3	441	449	7	12	3	245	251
3	19	2	201	196	6	20	2	250	269	10	11	2	108	111	4	6	3	168	172	7	13	3	-59	12
3	20	2	68	68	6	21	2	162	175	10	12	2	95	113	4	7	3	278	265	7	14	3	104	114
3	21	2	201	218	6	22	2	73	100	10	13	2	-49	54	4	8	3	416	430	7	15	3	115	113
3	22	2	234	230	6	23	2	124	146	10	14	2	65	73	4	9	3	526	505	7	16	3	235	240
3	23	2	164	175	6	24	2	111	120	10	15	2	74	71	4	10	3	260	250	7	17	3	94	95
3	24	2	-65	27	6	25	2	124	150	10	16	2	43	48	4	11	3	135	146	7	18	3	201	209
3	25	2	146	151	6	26	2	59	70	10	17	2	68	79	4	12	3	547	540	7	19	3	111	126
3	26	2	-59	44	6	27	2	41	102	11	18	2	240	259	4	13	3	498	495	7	20	3	53	49
3	27	2	82	87	7	0	2	265	247	11	1	2	95	113	4	14	3	177	170	7	21	3	97	105
3	28	2	-50	29	7	1	2	171	175	11	2	2	67	74	4	15	3	209	188	7	22	3	136	139
3	29	2	59	46	7	2	2	103	92	11	3	2	117	126	4	16	3	241	266	7	23	3	43	38
3	30	2	41	59	7	3	2	274	273	11	4	2	141	144	4	17	3	204	190	7	24	3	-29	22
4	0	2	173	176	7	4	2	131	136	11	5	2	103	106	4	18	3	66	90	8	0	3	84	76
4	1	2	845	878	7	5	2	-65	46	11	6	2	-48	37	4	19	3	120	118	8	1	3	132	120
4	2	2	458	454	7	6	2	133	134	11	7	2	80	78	4	20	3	118	127	8	2	3	146	170
4	3	2	749	765	7	7	2	141	126	11	8	2	-45	24	4	21	3	158	150	8	3	3	89	98
4	4	2	176	183	7	8	2	94	104	11	9	2	91	96	4	22	3	79	66	8	4	3	120	107
4	5	2	500	514	7	9	2	-67	76	11	10	2	-40	38	4	23	3	86	68	8	5	3	167	171
4	6	2	543	519	7	10	2	268	357	11	11	2	50	44	4	24	3	52	63	8	6	3	274	263
4	7	2	475	506	7	11	2	76	79	11	12	2	-34	21	4	25	3	106	125	8	7	3	131	126
4	8	2	432	409	7	12	2	209	195	11	13	2	49	67	4	26	3	61	85	8	8	3	224	236
4	9	2	137	78	7	13	2	97	114	12	14	2	65	75	4	27	3	72	74	8	9	3	101	103
4	10	2	395	367	7	14	2	315	332	12	15	2	68	80	4	28	3	50	70	8	10	3	258	244
4	11	2	246	260	7	15	2	305	282	12	16	2	82	88	5	0	3	228	218	8	11	3	127	136
4	12	2	393	370	7	16	2	142	165	12	17	2	49	63	5	1	3	185	172	8	12	3	147	179
4	13	2	194	178	7	17	2	-65	34	2	0	3	594	622	5	2	3	113	109	8	13	3	95	86
4	14	2	98	113	7	18	2	191	187	2	1	3	774	837	5	3	3	257	248	8	14	3	159	157
4	15	2	164	149	7	19	2	255	269	2	2	3	658	712	5	4	3	431	426	8	15	3	98	106
4	16	2	318	318	7	20	2	102	123	2	3	3	474	478	5	5	3	336	308	8	16	3	122	134
4	17	2	300	295	7	21	2	79	95	2	4	3	492	497	5	6	3	198	192	8	17	3	117	133
4	18	2	96	117	7	22	2	49	105	2	5	3	414	428	5	7	3	451	462	8	18	3	106	120
4	19	2	167	165	7	23	2	72	73	2	6	3	293	279	5	8	3	596	595	8	19	3	89	82
4	20	2	63	69	7	24	2	112	122	2	7	3	410	374	5	9	3	85	96	8	20	3	81	86
4	21	2	166	172	7	25	2	90	102	2	8	3	396	361	5	10	3	343	323	8	21	3	41	50
4	22	2	-57	8	8	0	2	90	85	2	9	3	226	217	5	11	3	345	318	8	22	3	53	57
4	23	2	152	159	8	1	2	161	160	2	10	3	226	202	5	12	3	319	299	8	0	3	-57	25
4	24	2	-62	65	8	2	2	107	97	2	11	3	237	244	5	13	3	134	124	9	1	3	-57	60
4	25	2	84	92	8	3	2	96	67	2	12	3	163	152	5	14	3	258	249	9	2	3	-57	43
4	26	2	-55	30	8	4	2	277	267	2	13	3	260	257	5	15	3	245	227	9	3	3	115	98
4	27	2	91	143	8	5	2	232	234	2	14	3	309	311	5	16	3	-59	41	9	4	3	98	92
4	28	2	87	106	8	6	2	234	213	2	15	3	225	218	5	17	3	94	105	9	5	3	114	101
4	29	2	-38	37	8	7	2	-68	27	2	16	3	251	227	5	18	3	78	110	9	6	3	146	139
5	0	2	-51	7	8	8	2	243	243	2	17	3	240	228	5	19	3	142	166	9	7	3	164	160
5	1	2	278	303	8	9	2	215	224	2	18	3	182	172	5	20	3	-57	30	9	8	3	194	195
5	2	2	364	374	8	10	2	280	238	2	19	3	355	363	5	21	3	78	86	9	9	3	65	65
5	3	2	477	603	8	11	2	-68	51	2	20	3	236	228	5	22	3	59	44	9	10	3	220	229
5	4	2	379	376	8	12	2	184	177	2	21	3	270	284	5	23	3	138	149	9	11	3	117	146
5	5	2	310	296	8	13	2	327	320	2	22	3	72	82	5	24	3	46	54	9	12	3	121	141
5	6	2	215	206	8	14	2	289	279	2	23	3	242	257	5	25	3	104	116	9	13	3	59	55
5	7	2	425	421	8	15	2	63	72	2	24	3	62	81	5	26	3	74	97	9	14	3	167	170
5	8	2	408	415	8	16	2	125	139	2	25	3	174	191	5	27	3	85	97	9	15	3	61	67
5	9	2	124	134	8	17	2	132	146	2	26	3	50	54	6	0	3	145	134	9	16	3	50	54
5	10	2	252	243	8	18	2	140	146	2	27	3	42	101	6	1	3	438	445	9	17	3	91	97
5	11	2	372	364	8	19	2	54	67	2	28	3	50	45	6	2	3	315	328	9	18	3	53	37
5	12	2	371	343	8	20	2	80	99	2	29	3	82	100	6	3	3	282	281	9	19	3	39	42
5	13	2	160	192	8	21	2	46	45	3	0	3	144	141	6	4	3	160	152	10	0	3	-50	8
5	14	2	279	274	8	22	2	59	73	3	1	3	633	704	6	5	3	322	299	10	1	3	138	131
5	15	2	-67	5	8	23	2	47	44	3	2	3	154	153	6	6	3	509	510	10	2	3	-50	29
5	16	2	206	200	9	0	2	101	96	3	3	3	700	717	6	7	3	119	98	10	3	3	156	152</

Table 2. Final coordinates in fractions of cell edges for selenium bis(diethylthiocarbamate). Origin halfway between three mutually perpendicular and non-intersecting screw axes. Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.4312 (2)	0.1154 (1)	-0.0561 (3)
S ₁	0.2778 (4)	0.0946 (2)	-0.3096 (7)
S ₂	0.2165 (5)	0.0609 (2)	0.1026 (7)
S ₃	0.5627 (4)	0.1588 (2)	-0.2972 (7)
S ₄	0.6630 (5)	0.1592 (2)	0.1216 (7)
N ₁	0.0534 (14)	0.0420 (5)	-0.2111 (22)
N ₂	0.7887 (11)	0.2095 (4)	-0.1790 (20)
C ₁	0.1687 (15)	0.0621 (5)	-0.1373 (24)
C ₂	0.0161 (16)	0.0436 (5)	-0.4295 (28)
C ₃	-0.0617 (19)	0.0928 (6)	-0.4799 (29)
C _{4A}	-0.0687 (44)	0.0287 (15)	-0.0727 (68)
C _{4B}	-0.0203 (35)	-0.0030 (14)	-0.0816 (64)
C _{5A}	-0.0754 (41)	-0.0308 (14)	-0.0751 (65)
C _{5B}	-0.1472 (49)	0.0296 (17)	-0.0143 (77)
C ₆	0.6828 (14)	0.1779 (5)	-0.1143 (24)
C ₇	0.8058 (15)	0.2251 (5)	-0.3956 (26)
C ₈	0.7416 (17)	0.2780 (6)	-0.4407 (32)
C ₉	0.8908 (14)	0.2295 (5)	-0.0308 (26)
C ₁₀	1.0143 (19)	0.1923 (7)	-0.0230 (31)

A and B indicate atoms in the two ethyl group configurations resulting from disorder.

Table 3. Components of atomic vibration tensors, $U \times 10^3$ in \AA^2 with standard deviations, referred to crystallographic axes. For Se and S the expression is $\exp\{-2\pi^2[U_{11}(ha^{-1})^2 + U_{22}(kb^{-1})^2 + U_{33}(lc^{-1})^2 + 2U_{12}hka^{-1}b^{-1} + 2U_{23}k lb^{-1}c^{-1} + 2U_{13}hla^{-1}c^{-1}]\}$. For the N and C atoms, the expression is $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$.

	U_{11}	(<i>U</i>)	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Se	48.31	(0.69)	46.63 (0.64)	53.95 (1.05)	- 2.96 (0.70)	4.45 (0.77)	-0.37 (1.06)
S ₁	51.81	(1.84)	57.35 (1.86)	54.66 (2.58)	- 9.16 (1.68)	6.15 (1.93)	5.22 (2.39)
S ₂	66.84	(2.35)	76.96 (2.44)	53.94 (2.79)	-10.32 (2.12)	14.17 (2.25)	-5.76 (3.11)
S ₃	51.24	(1.92)	68.13 (2.07)	54.84 (2.53)	-13.09 (1.97)	2.72 (2.03)	-4.46 (2.72)
S ₄	67.43	(2.36)	71.51 (2.34)	46.56 (2.48)	- 8.12 (2.05)	8.34 (2.10)	-6.32 (2.81)
N ₁	65.27	(3.53)					
N ₂	45.30	(2.76)					
C ₁	50.56	(3.66)					
C ₂	58.61	(3.82)					
C ₃	80.24	(4.93)					
C _{4A}	77.63	(10.13)					
C _{4B}	69.96	(9.47)					
C _{5A}	82.63	(10.31)					
C _{5B}	110.83	(15.35)					
C ₆	46.59	(3.40)					
C ₇	52.57	(3.68)					
C ₈	73.24	(4.76)					
C ₉	54.88	(3.76)					
C ₁₀	81.91	(5.44)					

Table 4. Bond lengths and angles in selenium bis(diethyldithiocarbamate) with standard deviations in brackets.

Se-S ₁	2.312(5) Å	∠S ₁ -Se-S ₂	70.9 (2)°
Se-S ₂	2.719(5)	∠S ₁ -Se-S ₃	87.7 (2)
Se-S ₃	2.332(4)	∠S ₁ -Se-S ₄	157.7 (2)
Se-S ₄	2.779(5)	∠S ₂ -Se-S ₃	158.5 (2)
S ₁ -C ₁	1.77(2)	∠S ₂ -Se-S ₄	131.5 (2)
S ₂ -C ₁	1.66(2)	∠S ₃ -Se-S ₄	70.0 (1)
S ₃ -C ₅	1.75(2)	∠Se-S ₁ -C ₁	91.2 (5)
S ₄ -C ₅	1.65(2)	∠Se-S ₂ -C ₁	80.4 (5)
C ₁ -N ₁	1.33(2)	∠Se-S ₃ -C ₅	91.1 (5)
C ₅ -N ₂	1.38(2)	∠Se-S ₄ -C ₅	78.8 (5)
N ₁ -C ₂	1.50(2)	∠S ₁ -C ₁ -S ₂	117.6 (9)
C ₂ -C ₃	1.50(2)	∠S ₁ -C ₁ -N ₁	116.6(12)
N ₁ -C _{4A}	1.54(5)	∠S ₂ -C ₁ -N ₁	125.8(12)
C _{4A} -C _{5A}	1.52(5)	∠S ₃ -C ₅ -S ₄	120.1 (8)
N ₁ -C _{4B}	1.60(4)	∠S ₃ -C ₅ -N ₂	116.3(11)
C _{4B} -C _{5B}	1.55(6)	∠S ₄ -C ₅ -N ₂	123.6(11)
N ₂ -C ₇	1.50(2)	∠C ₁ -N ₁ -C ₂	123.5(13)
C ₇ -C ₈	1.52(2)	∠C ₁ -N ₁ -C _{4A}	120.9(20)
N ₂ -C ₉	1.49(2)	∠C ₁ -N ₁ -C _{4B}	117.0(18)
C ₉ -C ₁₀	1.53(2)	∠C ₂ -N ₁ -C _{4A}	113.6(19)
		∠C ₂ -N ₁ -C _{4B}	115.7(17)
		∠N ₁ -C ₂ -C ₃	111.2(13)
		∠N ₁ -C _{4A} -C _{5A}	104.2(29)
		∠N ₁ -C _{4B} -C _{5B}	97.3(26)
		∠C ₅ -N ₂ -C ₇	122.5(12)
		∠C ₅ -N ₂ -C ₉	119.4(13)
		∠C ₇ -N ₂ -C ₉	118.1(11)
		∠N ₂ -C ₇ -C ₈	112.3(13)
		∠N ₂ -C ₉ -C ₁₀	109.4(12)

As mentioned before, there are two different configurations of the C₄-C₅ ethyl group. They correspond to a rotation of about 150° around the N₁-C₄ bond. Due probably to steric effects (Fig. 2, Table 5), both carbon atoms of this ethyl group occupy different positions in the two configurations. In the configuration A, the molecules nearly have mirror plane symmetry, the mirror plane passes through the selenium atom at right angles to the SeS₄ plane. There are probably a 1:1 mixture of A and B molecules statistically distributed in the crystals.

The molecules are approximately planar, apart from the disordered ethyl group, the methyl groups and the hydrogen atoms. The least squares plane through this roughly planar part of the molecule is within 0.12 Å of any of the atoms defining it. The atoms C_{4A} and C_{4B} are -0.56 and 0.37 Å, respectively, away from this plane. For the normal to the least squares plane through the SeS₄ group with all atoms given equal weight, the equation $0.500x - 0.849y - 0.165z = 0$ referred to the crystal axes, is found. The plane is -0.369 Å from the origin, while Se, S₁, S₂, S₃, and S₄ are 0.022, 0.007, -0.014, 0.016, and 0.001 Å, respectively, away from the plane.

In Fig. 3 the nearly planar part of the molecule is shown projected into the SeS₄ plane with bond lengths and angles included. The configuration

Table 5. Intramolecular contacts.

Se-C ₁	2.94 Å	C ₁ -C _{4A}	2.50 Å
Se-C ₄	2.94	C ₁ -C _{4B}	2.50
S ₁ -S ₂	2.94	C ₁ -C _{5A}	3.38
S ₁ -S ₃	3.22	C ₁ -C _{5B}	3.28
S ₁ -N ₁	2.64	C ₂ -C _{4A}	2.54
S ₁ -C ₂	2.97	C ₂ -C _{4B}	2.63
S ₁ -C ₃	3.49	C ₂ -C _{5A}	3.16
S ₂ -N ₁	2.67	C ₂ -C _{5B}	3.21
S ₂ -C _{4A}	3.12	C ₃ -C _{4A}	3.17
S ₂ -C _{4B}	3.07	C ₃ -C _{4B}	3.63
S ₂ -C _{5A}	3.86	C ₃ -C _{5A}	4.15
S ₂ -C _{5B}	3.70	C ₃ -C _{5B}	3.59
S ₃ -S ₄	2.95	C ₆ -C ₇	2.53
S ₃ -N ₂	2.67	C ₆ -C ₈	3.40
S ₃ -C ₇	2.98	C ₆ -C ₉	2.48
S ₃ -C ₈	3.63	C ₆ -C ₁₀	3.30
S ₄ -N ₂	2.67	C ₇ -C ₉	2.57
S ₄ -C ₉	3.02	C ₇ -C ₁₀	3.31
S ₄ -C ₁₀	3.64	C ₈ -C ₉	3.33
N ₁ -C ₃	2.48		
N ₁ -C _{5A}	2.42		
N ₁ -C _{5B}	2.37		
N ₂ -C ₈	2.51		
N ₂ -C ₁₀	2.46		
C ₁ -C ₂	2.49		
C ₁ -C ₃	3.29		

Table 6. Intermolecular distances in Å.

C ₂ -C _{5B}	3/2-x, -y, -1/2+z	4.08	C ₆ -C ₁₀	»	3.81
C ₃ -C _{5A}	»	3.91	C ₉ -C ₁₀	»	4.18
C _{5B} -C _{5B}	»	4.17	C ₈ -C ₁₀	»	3.87
S ₁ -C ₈	-1/2+x, 1/2-y, 1-z	3.67	C ₃ -C _{5B}	x, y, -1+z	3.99
S ₃ -C ₈	»	3.92	S ₁ -C _{4B}	1/2-x, -y, -1/2+z	3.78
S ₂ -C ₁₀	-1+x, y, z	3.98	S ₁ -C _{5A}	»	3.76
C ₁ -C ₁₀	»	3.73	S ₃ -C _{5A}	»	3.76
C ₃ -C ₆	»	4.10	S ₂ -C ₁	1/2-x, -y, 1/2+z	3.76
C ₃ -C ₇	»	3.66	S ₂ -C ₂	»	3.73
C ₃ -C ₁₀	»	4.03	S ₂ -C _{4B}	»	3.91
C ₃ -N ₂	»	3.87	S ₂ -N ₁	»	3.67
C _{5B} -C _{5B}	3/2-x, -y, 1/2+z	4.17	S ₄ -C _{5A}	»	3.94
C _{5A} -C _{5B}	»	3.98	C ₁₀ -N ₂	1/2+x, 1/2-y, -z	3.90
Se-C ₉	-1/2+x, 1/2-y, -z	4.02	S ₂ -C ₂	x, y, 1+z	3.70
S ₃ -C ₉	»	3.96	S ₂ -C ₃	»	3.96
S ₄ -C ₉	»	3.93	S ₁ -C ₇	»	3.88
C ₆ -C ₉	»	3.82	S ₄ -C _{5B}	1+x, y, z	3.89

The left column represents distances from an atom in the original molecule (Table 2) to an atom in a molecule whose transformation from the original one is listed in the next column.

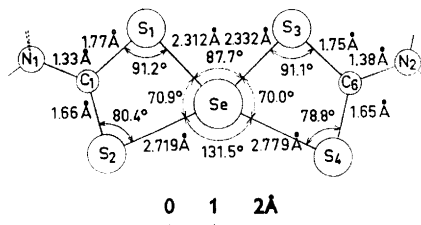


Fig. 3. The projection of the central part of the molecule as seen along the normal to the least squares plane through the nearly planar SeS_4 group.

around the central selenium atom resembles that found for divalent tellurium in tellurium di(ethylxanthate)⁵ and tellurium di(morpholyldithiocarbamate).⁸ However, in the two tellurium compounds, there are short intermolecular $\text{Te}\cdots\text{S}$ contacts. No corresponding $\text{Se}\cdots\text{S}$ contact is found in the present structure.

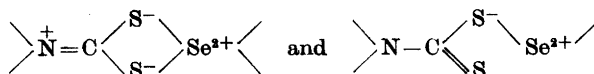
There are two long and two short $\text{Se}-\text{S}$ bonds, the bond lengths being $\text{Se}-\text{S}_1 = 2.312 \pm 0.005$ Å, $\text{Se}-\text{S}_2 = 2.719 \pm 0.005$ Å, $\text{Se}-\text{S}_3 = 2.332 \pm 0.004$ Å, and $\text{Se}-\text{S}_4 = 2.779 \pm 0.005$ Å. These values are all significantly larger than the covalent radii sum of 2.21 Å.¹⁸ The inter-ligand $\text{Se}-\text{S}$ bond angles are $\angle \text{S}_1-\text{Se}-\text{S}_3 = 87.7 \pm 0.2^\circ$ and $\angle \text{S}_2-\text{Se}-\text{S}_4 = 131.5 \pm 0.2^\circ$. The corresponding angles in the two tellurium analogs^{5,8} are close to 82 and 145° , respectively, reflecting the greater size of the tellurium atom as compared to selenium. Replacing tellurium by selenium in these compounds results in shorter central atom to S_1 and S_3 bond lengths. The inter-ligand $\text{S}_1\cdots\text{S}_3$ contact therefore becomes too short unless the $\text{S}_1-\text{Se}-\text{S}_3$ angle opens up. As a consequence of this effect and a similar increase in the intra-ligand sulphur to central atom bond angles from about 66° to close to 70° , the other, large inter-ligand bond angle is then reduced as found above. Another result of replacing tellurium by selenium is that the *trans* three-center $\text{S}_1-\text{Se}-\text{S}_4$ and $\text{S}_3-\text{Se}-\text{S}_2$ systems become less bent, both angles being close to 158° as compared to values between 147.4 and 149.8° found in their tellurium counterparts.^{5,8}

The lengths of the nearly linear three-center $\text{Se}-\text{Se}-\text{Se}$ systems in potassium and rubidium triselenocyanate, 5.34 and 5.30 Å, respectively,⁹⁻¹² assuming single covalent radii for the outer selenium atoms, give an average bonding radius of 1.49 Å for the central selenium atom. The *trans* three-center $\text{S}-\text{Se}-\text{S}$ systems in the present structure have an average length of 5.072 Å, which, with single covalent radii for the ligand sulphur atoms, corresponds to a bonding radius of 1.496 Å for selenium. This value is thus close to that found for selenium in the triselenocyanate ion.⁹⁻¹² A corresponding agreement has been found between the tellurium radius in linear three-center systems and in the non-linear three-center systems in tellurium di(ethylxanthate)⁵ and tellurium di(morpholyldithiocarbamate).⁸ As in the tellurium analogs, *p*-orbitals probably play an important role in the bonding in the SeS_4 group.

The recent structure determination of phenylarsenic bis(diethyldithiocarbamate)²⁰ shows that apart from the phenyl group, the configuration around the central arsenic atom is very close to that found for selenium in the present work, except that the AsS_4 group is slightly pyramidal. This similarity is perhaps not so surprising taking into account that arsenic(III) with a phenyl

substituent is isoelectronic with selenium(II). The structure of arsenic tris(diethylthiocarbamate)²¹ is distorted trigonal antiprismatic. The short and long As-S bonds of average lengths 2.35 Å and 2.8–2.9 Å appear not to be significantly different from those found in phenylarsenic bis(diethylthiocarbamate).²⁰ In both arsenic compounds and in selenium bis(diethylthiocarbamate), the bond angles between the short As-S or Se-S bonds are all close to 90°. This supports the idea that the sulphur to central atom bonding in such compounds is based mainly on *p*-orbitals, perhaps with some *s*-orbital contribution. Each long sulphur to central atom bond might be pictured as part of a non linear (145–160° angle), asymmetric three-center system, each long bond being *trans* to a short one.

The short and long C-S bond lengths in selenium bis(diethylthiocarbamate) have average values of 1.66 and 1.76 Å, respectively, while the C...N bond lengths have an average value of 1.35 Å. These bond lengths are normal for dithiocarbamates²² and imply that the canonical forms indicated



above are the most important ones. The angles at the N₁, N₂, C₁, and C₆ atoms correspond to *sp*² hybridization in agreement with the above. Other N-C and C-C bond lengths correspond to normal, covalent bond lengths within the error limits.

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