

The Crystal and Molecular Structure of Selenium Di(morpholyldithiocarbamate)

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The crystal and molecular structure of selenium di(morpholyldithiocarbamate), $\text{Se}[\text{OC}_4\text{H}_8\text{NCS}_2]_2$, has been determined from three-dimensional X-ray data collected by multiple-film techniques using $\text{CuK}\alpha$ radiation. The material crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell, with $a=10.976(3)$ Å, $b=15.707(3)$ Å, $c=9.125(2)$ Å, and $\beta=92.17(2)^\circ$. The observed and calculated densities are 1.66 and 1.70 g/cm³, respectively. Full-matrix least squares refinement of the structure has yielded a final value for the conventional R -factor of 0.093 for 1097 visually estimated reflections. The monomeric molecules are nearly planar, with each selenium atom surrounded by a distorted square planar arrangement of sulfur atoms. There are two short and two long Se-S bonds, each short bond being *trans* to a long one at interbond angles close to 155° . The bond lengths are $\text{Se}-\text{S}_1=2.282(6)$ Å, $\text{Se}-\text{S}_2=2.782(5)$ Å, $\text{Se}-\text{S}_3=2.314(6)$ Å, and $\text{Se}-\text{S}_4=2.791(6)$ Å. The corresponding angles are $\text{S}_1-\text{Se}-\text{S}_2=70.5(2)^\circ$, $\text{S}_1-\text{Se}-\text{S}_3=84.6(2)^\circ$, $\text{S}_3-\text{Se}-\text{S}_4=69.7(2)^\circ$, and $\text{S}_2-\text{Se}-\text{S}_4=135.0(2)^\circ$.

This work is part of a study of compounds of divalent selenium and tellurium with dithio and related anions.¹⁻⁹ The earlier studies have shown the tendency of bidentate dithio ligands to form complexes of distorted square-planar geometry with Te(II) and Se(II). The present study confirms this tendency.

EXPERIMENTAL SECTION

Selenium di(morpholyldithiocarbamate) was prepared by the reaction of stoichiometric amounts of sodium monoselenopentathionate with sodium morpholyldithiocarbamate in aqueous solution.¹⁰ Recrystallization from an ethanol-benzene mixture yielded small yellow prisms. Oscillation and Weissenberg photographs established that the crystals belonged to the monoclinic system, and were in fact isomorphous with the tellurium(II) complex of the same ligand.⁸ This established the space group as $P2_1/n$. Cell parameters were determined at ambient temperature by measurement of 2θ for 34 high-order reflections on NaCl-calibrated $0kl$ and $h0l$ Weissenberg photographs employing $\text{CuK}\alpha$ radiation. Refinement by a least squares program gave final values of $a=10.976(3)$ Å, $b=15.707(3)$ Å, $c=9.125(2)$ Å, and $\beta=92.17(2)^\circ$. There are four molecules

Table 1. Observed and calculated $hk0$ and $0kl-3kl$ 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)	H	K	L	F(O)	F(C)
0	2	0	555	-585	0	4	5	341	-397	1	12	0	117	-122	1	11	5	223	218	1	13	-1	-55	24
0	4	0	264	-214	0	9	5	38	-75	1	13	0	254	242	1	12	5	134	-122	1	14	-1	-57	24
0	6	0	648	637	0	10	5	145	137	1	14	0	265	-255	1	13	5	-57	32	1	15	-1	-57	9
0	8	0	609	-565	0	11	5	168	-192	1	15	0	147	-119	1	14	5	-54	15	1	16	-1	-212	-205
0	10	0	675	-628	0	12	5	105	-121	1	16	0	64	94	1	15	5	113	-124	1	17	-1	-142	130
0	12	0	613	639	0	13	5	87	95	1	17	0	64	97	1	16	5	45	56	1	18	-1	-66	-19
0	14	0	230	-248	0	14	5	171	-212	1	18	0	-47	38	1	17	5	62	58	1	19	-1	-39	-35
0	16	0	-38	-15	0	15	5	35	36	1	19	0	-39	40	1	1	6	167	-145	1	20	-1	64	92
0	18	0	118	130	0	16	5	38	56	1	20	0	31	-38	1	2	6	266	-284	1	1	-2	698	-672
0	20	0	63	72	0	17	5	48	-67	1	0	1	897	802	1	3	6	312	352	1	2	-2	411	-360
0	1	1	642	690	0	18	5	30	50	1	1	1	864	-936	1	4	6	269	295	1	3	-2	545	-555
0	2	1	199	188	0	0	6	201	201	1	2	1	713	771	1	5	6	185	-202	1	4	-2	277	231
0	3	1	2316	-1917	0	1	6	342	-351	1	3	1	1677	1628	1	6	6	255	273	1	5	-2	391	-383
0	4	1	690	770	0	2	6	314	-314	1	4	1	1393	-1402	1	7	6	299	-321	1	6	-2	104	-145
0	5	1	288	306	0	4	6	124	169	1	5	1	1401	1560	1	8	6	164	-140	1	7	-2	872	843
0	6	1	116	108	0	5	6	530	631	1	6	1	699	687	1	9	6	165	160	1	8	-2	42	-30
0	7	1	209	261	0	6	6	178	-163	1	7	1	294	-261	1	10	6	-158	86	1	9	-2	143	-138
0	8	1	259	-311	0	7	6	214	-200	1	8	1	528	-509	1	11	6	-58	-27	1	10	-2	126	132
0	9	1	765	-921	0	8	6	50	-58	1	9	1	186	-183	1	12	6	86	74	1	11	-2	103	-95
0	10	1	40	-67	0	9	6	295	-331	1	10	1	220	-233	1	13	6	191	-195	1	12	-2	96	-103
0	11	1	166	-180	0	10	6	154	-176	1	11	1	503	499	1	14	6	108	-119	1	13	-2	469	494
0	12	1	124	-131	0	11	6	231	302	1	12	1	218	222	1	15	6	44	44	1	14	-2	766	746
0	13	1	239	261	0	12	6	119	113	1	13	1	498	-495	1	16	6	37	-16	1	15	-2	-57	-33
0	14	1	-39	-14	0	13	6	191	-234	1	14	1	57	28	1	17	6	-57	17	1	16	-2	155	158
0	15	1	123	-132	0	14	6	98	-140	1	15	1	-57	12	1	0	7	653	-670	1	17	-2	226	-223
0	16	1	38	-67	0	15	6	68	-99	1	16	1	229	-216	1	1	7	455	-476	1	18	-2	77	-75
0	17	1	56	-60	0	16	6	59	89	1	17	1	-52	15	1	2	7	292	296	1	19	-2	111	119
0	18	1	-32	72	0	17	6	83	72	1	18	1	133	124	1	3	7	242	236	1	20	-2	804	766
0	19	1	130	167	0	1	7	175	-174	1	19	1	-38	-10	1	4	7	186	167	1	1	-3	680	680
0	20	1	-18	-1	0	2	7	391	-425	1	20	1	-24	-5	1	5	7	406	387	1	2	-3	565	-511
0	2	2	979	697	0	3	7	-37	52	1	1	2	309	-210	1	6	7	-57	-16	1	3	-3	322	-302
0	1	2	85	-36	0	4	7	496	567	1	2	2	459	370	1	7	7	284	-288	1	4	-3	950	-774
0	2	2	124	-108	0	5	7	165	208	1	3	2	145	-205	1	7	7	158	75	1	5	-3	143	-138
0	3	2	170	-201	0	6	7	235	262	1	4	2	769	740	1	9	7	-57	11	1	6	-3	800	904
0	4	2	709	-776	0	7	7	89	82	1	5	2	526	483	1	10	7	384	396	1	7	-3	78	48
0	5	2	68	-90	0	8	7	194	-278	1	6	2	695	662	1	11	7	98	98	1	8	-3	-45	15
0	6	2	980	1058	0	9	7	-39	-5	1	7	2	702	696	1	12	7	219	-213	1	9	-3	193	179
0	7	2	730	811	0	10	7	278	319	1	8	2	628	-643	1	13	7	124	-149	1	10	-3	132	-136
0	8	2	124	115	0	11	7	129	142	1	9	2	267	-256	1	14	7	-42	18	1	11	-3	343	-342
0	9	2	187	-191	0	12	7	35	-51	1	10	2	74	-68	1	15	7	-35	-3	1	12	-3	241	230
0	10	2	97	-134	0	13	7	35	-85	1	11	2	-51	-33	1	16	7	-23	39	1	13	-3	57	42
0	11	2	241	265	0	14	7	125	-176	1	12	2	170	187	1	1	8	440	-451	1	14	-3	-57	29
0	12	2	91	115	0	15	7	-24	-2	1	13	2	242	237	1	2	8	338	-373	1	15	-3	56	-25
0	13	2	119	138	0	16	7	24	57	1	14	2	338	-332	1	3	8	174	204	1	16	-3	183	-185
0	14	2	217	243	0	0	8	255	-305	1	15	2	213	-229	1	4	8	176	186	1	17	-3	48	-52
0	15	2	161	-192	0	1	8	172	-187	1	16	2	70	-58	1	5	8	84	-91	1	18	-3	-42	21
0	16	2	250	-287	0	2	8	191	194	1	17	2	-50	26	1	6	8	61	-36	1	19	-3	-32	-8
0	17	2	-34	38	0	3	8	90	-95	1	18	2	106	104	1	7	8	150	-137	1	1	-4	735	712
0	18	2	88	113	0	4	8	128	-123	1	19	2	-26	10	1	8	8	55	-23	1	2	-4	1261	1163
0	19	2	124	115	0	5	8	93	131	1	20	2	267	-256	1	9	8	291	305	1	3	-4	580	608
0	20	2	-12	32	0	6	8	-39	-39	1	1	3	273	219	1	10	8	107	137	1	4	-4	523	-499
0	1	3	368	347	0	7	8	139	-167	1	2	3	865	-814	1	11	8	-47	-3	1	5	-4	201	185
0	2	3	749	-720	0	8	8	81	-93	1	3	3	704	-647	1	12	8	43	-34	1	6	-4	404	411
0	3	3	928	-993	0	9	8	49	-71	1	4	3	394	-357	1	13	8	81	-75	1	7	-4	224	210
0	4	3	498	-502	0	10	8	128	172	1	5	3	583	577	1	14	8	32	-48	1	8	-4	580	608
0	5	3	367	366	0	11	8	134	183	1	6	3	469	472	1	0	9	-55	-33	1	9	-4	308	-308
0	6	3	-27	68	0	12	8	-29	-11	1	7	3	226	-250	1	1	9	95	-63	1	10	-4	378	-379
0	7	3	146	207	0	13	8	38	-43	1	8	3	174	-184	1	2	9	-54	5	1	11	-4	144	-120
0	8	3	352	-360	0	1	9	-37	11	1	9	3	131	-154	1	3	9	96	-96	1	12	-4	-58	-18
0	9	3	207	-192	0	2	9	-37	5	1	10	3	-51	-4	1	4	9	187	177	1	13	-4	249	256
0	10	3	194	-198	0	3	9	48	64	1	11	3	323	352	1	5	9	57	60	1	14	-4	106	101
0	11	3	37	72	0	4	9	-37	-35	1	12	3	360	343	1	6	9	170	-177	1	15	-4	99	-105
0	12	3	203	213	0	5	9	-36	-10	1	13	3	137	116	1	7	9	114	-114	1	16	-4	91	-101
0	13	3	232	280	0	6	9	48	46	1	14	3	180	-166	1	8	9	-47	-4	1	17	-4	-44	-24
0	14	3	102	-116	0	7	9	115	-146	1	15	3	306	-325	1	9	9	44	50	1	18	-4	-36	36
0	15	3	114	-114	0	8	9	88	-137	1	16	3	68	75	1	10	9	124	112	1	19	-4	-20	89
0	16	3	-36	-19	0	9	9	-31	6	1	17	3	150	144	1	11	9	-36	29	1	0	-5	915	886
0	17	3	53	-44	0	10	9	-28	-17	1	18	3	-41	36	1	12	9	32	27	1	1	-5	57	63
0	18	3	94	121	0	11	9	44	64	1	1	4	307	296	1	1	10	-47	-29	1	2	-5	115	102
0	19	3	-22																					

Table 1. Continued.

Table with 16 columns: 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). The table contains numerical data for various indices and values, organized in four groups of four columns each.

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)				
3 10	5	221	177		3 0	-1	365	-323		3 3	-5	390	-345		3 5	-10	121	108					
3 11	5	80	78		3 1	-1	333	-292		3 6	-10	93	-371		3 6	-10	93	-86					
3 12	5	258	-227		3 2	-1	265	211		3 5	-5	379	377		3 7	-10	-47	36					
3 13	5	-71	-44		3 3	-1	239	-248		3 6	-5	304	293		3 8	-10	110	136					
3 14	5	-67	13		3 4	-1	188	-152		3 7	-5	775	-842		3 9	-10	216	-141					
3 15	5	-61	34		3 5	-1	274	219		3 8	-5	141	86		3 0	-11	-43	-47					
3 16	5	97	94		3 6	-1	344	319		3 9	-5	299	257		3 1	-11	85	115					
3 17	5	85	80		3 7	-1	71	-7		3 10	-5	270	-251		3 2	-11	-42	11					
3 1	6	123	101		3 8	-1	191	-150		3 11	-5	129	95		3 3	-11	-40	-54					
3 2	6	238	181		3 9	-1	602	-601		3 12	-5	-74	-19		3 4	-11	75	-91					
3 3	6	163	153		3 10	-1	-61	-37		3 13	-5	-72	31		1	1	0	426	588				
3 4	6	94	-450		3 11	-1	616	624		3 14	-5	161	123		2	0	0	149	-99				
3 5	6	-71	-18		3 12	-1	-69	46		3 15	-5	-62	28		2	1	0	1522	-1794				
3 6	6	125	105		3 13	-1	184	166		3 16	-5	207	-206		4	0	0	287	301				
3 7	6	259	-227		3 14	-1	246	201		3 17	-5	89	81		4	1	0	104	-136				
3 8	6	80	145		3 15	-1	253	-249		3 18	-5	284	249		4	2	0	48	-79				
3 9	6	143	147		3 16	-1	89	-80		3 2	-6	469	-380		4	3	0	380	-442				
3 10	6	166	-148		3 17	-1	154	125		3 3	-6	529	-525		4	4	0	102	148				
3 11	6	139	126		3 18	-1	-56	45		3 4	-6	110	58		4	5	0	567	543				
3 12	6	-70	-15		3 19	-1	-44	36		3 5	-6	-69	103		4	6	0	138	136				
3 13	6	170	-157		3 1	-2	176	-175		3 6	-6	326	-219		4	7	0	539	-543				
3 14	6	-60	-68		3 2	-2	1166	-1230		3 7	-6	174	174		4	8	0	375	-340				
3 15	6	-52	-24		3 3	-2	866	-876		3 8	-6	-73	-4		4	9	0	252	-250				
3 16	6	-42	22		3 4	-2	695	731		3 9	-6	166	-148		4	10	0	163	152				
3 17	6	172	-186		3 5	-2	171	125		3 10	-6	121	113		4	11	0	203	215				
3 18	6	259	-227		3 6	-2	252	234		3 11	-6	-73	-28		4	12	0	125	122				
3 19	6	93	-38		3 7	-2	503	473		3 12	-6	-70	2		4	13	0	178	161				
3 20	6	-73	44		3 8	-2	662	690		3 13	-6	200	146		4	14	0	155	-172				
3 1	7	221	185		3 9	-2	77	-54		3 14	-6	-61	58		4	15	0	191	-192				
3 2	7	100	94		3 10	-2	352	313		3 15	-6	102	-91		4	16	0	296	258				
3 3	7	177	-159		3 11	-2	213	202		3 16	-6	97	85		4	17	0	181	163				
3 4	7	71	71		3 12	-2	-71	-11		3 17	-6	179	160		5	1	0	272	-27				
3 5	7	-74	-16		3 13	-2	209	172		3 1	-7	-70	41		5	2	0	439	-490				
3 6	7	186	153		3 14	-2	221	-176		3 2	-7	129	-116		5	3	0	498	504				
3 7	7	76	54		3 15	-2	184	-164		3 3	-7	100	94		5	4	0	-67	-19				
3 8	7	182	-143		3 16	-2	-88	27		3 4	-7	262	-276		5	5	0	126	115				
3 9	7	-62	-86		3 17	-2	84	-72		3 5	-7	432	-436		5	6	0	342	-290				
3 10	7	359	279		3 18	-2	90	80		3 6	-7	185	209		5	7	0	485	-486				
3 11	7	127	-118		3	0	-3	1572	1602		3 7	-7	214	198		5	8	0	317	-332			
3 12	7	-37	-15		3 1	-3	1130	-1087		3 8	-7	119	95		5	9	0	196	188				
3 13	7	174	-156		3 2	-3	951	-946		3 9	-7	125	-118		5	10	0	232	212				
3 14	7	237	218		3 3	-3	453	418		3 10	-7	-70	-18		5	11	0	324	305				
3 15	7	311	280		3 4	-3	208	-132		3 11	-7	-67	-3		5	12	0	286	262				
3 16	7	140	-135		3 5	-3	814	860		3 12	-7	120	65		5	13	0	369	-354				
3 17	7	167	-147		3 6	-3	695	659		3 13	-7	-57	38		5	14	0	193	-45				
3 18	7	77	-25		3 7	-3	-57	-11		3 14	-7	106	83		5	15	0	-42	133				
3 19	7	-70	-9		3 8	-3	133	-111		3 1	-8	118	65		5	16	0	79	85				
3 20	7	458	215		3 9	-3	456	-134		3 2	-8	264	270		5	17	0	96	86				
3 1	8	186	173		3 10	-3	274	-234		3 3	-8	132	-111		6	1	0	750	-809				
3 2	8	111	-110		3 11	-3	339	289		3 4	-8	-72	-54		6	2	0	257	-240				
3 3	8	-56	10		3 12	-3	438	437		3 5	-8	-72	-10		6	3	0	179	237				
3 4	8	65	-62		3 13	-3	321	-316		3 6	-8	-71	34		6	4	0	317	-254				
3 5	8	-42	-15		3 14	-3	210	-193		3 7	-8	155	155		6	5	0	429	450				
3 6	8	311	281		3 15	-3	122	-95		3 8	-8	194	172		6	6	0	498	-548				
3 7	8	118	100		3 16	-3	-65	-9		3 9	-8	85	-86		6	7	0	629	-647				
3 8	8	-68	62		3 17	-3	107	89		3 10	-8	-62	-42		6	8	0	174	169				
3 9	8	91	63		3 18	-3	-49	15		3 11	-8	88	-63		6	9	0	192	8				
3 10	8	-66	41		3 1	-4	254	266		3 12	-8	104	-92		6	10	0	105	-117				
3 11	8	294	-252		3 2	-4	736	-675		3 13	-8	112	109		6	11	0	426	413				
3 12	8	140	-114		3 3	-4	527	-500		3 14	-8	40	45		6	12	0	-102	-48				
3 13	8	211	204		3 4	-4	430	358		3	0	-9	412		6	13	0	288	-289				
3 14	8	-57	49		3 5	-4	127	100		3 1	-9	195	196		6	14	0	-95	-47				
3 15	8	-52	-9		3 6	-4	174	145		3 2	-9	213	-186		6	15	0	-90	-81				
3 16	8	110	101		3 7	-4	259	230		3 3	-9	136	131		6	16	0	116	108				
3 17	8	46	-56		3 8	-4	204	-182		3 4	-9	-67	-31		6	17	0	176	164				
3 18	8	-57	20		3 9	-4	464	-465		3 5	-9	142	-145		6	18	0	-60	-3				
3 19	8	76	68		3 10	-4	180	123		3 6	-9	83	76		7	1	0	464	-470				
3 20	8	150	131		3 11	-4	175	-139		3 7	-9	87	92		7	2	0	552	597				
3 1	9	113	-113		3 12	-4	142	138		3 8	-9	117	-100		7	3	0	252	244				
3 2	9	59	-65		3 13	-4	260	201		3 9	-9	100	94		7	4	0	647	-707				
3 3	9	56	-72		3 14	-4	262	-209		3 10	-9	150	-161		7	5	0	99	-94				
3 4	9	70	48		3 15	-4	-68	-8		3 11	-9	111	-119		7	6	0	89	-106				
3 5	9	80	72		3 16	-4	-61	51		3 12	-9	101	122		7	7	0	299	-300				
3 6	9	-11	-46		3 17	-4	-53	-25		3 13	-9	153	145		7	8	0	272	239				
3 7	9	111	89		3 18	-4	508	469		3 14	-9	182	191		7	9	0	184	194				
3 8	9	87	90		3 1	-5	465	-429		3 15	-9	105	-112		7	10	0	229	-174				
3 9	9	-35	29		3 2	-5	282	275		3 16	-9	188	-194		7	11	0	-102	50				
																			14	0	57	-53	
																			14	1	0	-46	-73

in the cell with density calc. 1.70, found 1.66 g/cm³. Thus, each molecule occupies one of the general positions of the space group, which are $\pm(x,y,z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

Two small crystals were selected for intensity data collection, the larger of which was approximately 0.07 × 0.10 × 0.25 mm³. Intensity data were collected from the $hk0$ and $0kl-3kl$ zones by means of zero-layer and equi-inclination Weissenberg techniques, employing Ni-filtered CuK radiation. Intensities were estimated visually from integrated multiple-film exposures by comparison with a standard film strip. Out of 1401 possible reflections, 1097 were observed and measured. The data were corrected for Lorentz, polarization, and secondary extinction effects. The dimensions of each crystal were carefully measured, and an absorption correction ($\mu=81.4$ cm⁻¹) was applied to the

data. Transmission factors ranged from 0.38 to 0.75. Most computations were carried out using a set of programs made available by the Weizmann Institute, Rehovoth, Israel, and modified for use on the University of Bergen's IBM 360-50H computer by Dr. Dove Rabinovich. The correction for secondary extinction and the final cycles of least squares refinement were carried out using programs designed by K. Maartmann-Moe of this Institute. The three-dimensional Fourier calculations were made using a program designed by E. Alver, also of this Institute.

STRUCTURE ANALYSIS

A three-dimensional Patterson map established the coordinates of the selenium atom in the asymmetric unit. Successive three-dimensional Fourier syntheses revealed the positions of all atoms in the molecule except hydrogen. Full matrix, least squares refinement with isotropic temperature factors was then started using a program which minimized the expression $\sum w[|F_o| - k|F_c|]^2 / \sum wF_o^2$, where k is the variable scale factor, and w , the relative weight assigned a reflection, is the inverse of the square of the standard deviation in the observed structure factor for that reflection.

After two cycles of refinement, the factor $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ reached a value of 0.13. Anisotropic temperature factors were then introduced for selenium and sulfur. Further refinement brought the R factor down to its final value of 0.093. The last cycles of refinement were computed by means of another full-matrix program which minimized the expression $\sum w[|F_c| - |F_o|]^2$, where w , the weight of a reflection, is defined by the expression $a/(a + b|F_o| + c|F_o|^2)$. Values used for the constants were $a = 1.0$, $b = 2.23 \times 10^{-2}$, and $c = 1.9 \times 10^{-4}$.

Atomic scattering factors for selenium, sulfur, oxygen, nitrogen, and carbon listed in *International Tables*¹¹ were used. The scattering factors for

Table 2. Atomic coordinates for selenium di(morpholyldithiocarbamate), in fractions of cell edges. Origin at a center of symmetry. Standard deviations in brackets.

	x	y	z
Se	0.0884 (3)	0.1577 (1)	0.0425 (2)
S ₁	0.2379 (6)	0.1737 (3)	-0.1224 (5)
S ₂	0.0388 (7)	0.0536 (3)	-0.1991 (5)
S ₃	0.2012 (7)	0.2549 (3)	0.1816 (5)
S ₄	-0.0156 (6)	0.1815 (3)	0.3140 (6)
O ₁	0.3720 (18)	0.0289 (8)	-0.6016 (14)
O ₂	0.1260 (16)	0.4428 (8)	0.6103 (14)
N ₁	0.2423 (20)	0.0724 (9)	-0.3544 (16)
N ₂	0.1358 (19)	0.2915 (9)	0.4530 (16)
C ₁	0.1760 (23)	0.0961 (11)	-0.2402 (19)
C ₂	0.3752 (26)	0.0963 (12)	-0.3663 (20)
C ₃	0.4029 (24)	0.1069 (12)	-0.5284 (20)
C ₄	0.2446 (29)	0.0091 (14)	-0.5992 (22)
C ₅	0.2044 (24)	-0.0043 (12)	-0.4439 (19)
C ₆	0.1006 (23)	0.2457 (11)	0.3337 (19)
C ₇	0.0596 (24)	0.2951 (11)	0.5814 (20)
C ₈	0.0176 (23)	0.3909 (11)	0.5907 (19)
C ₉	0.2050 (26)	0.4385 (13)	0.4841 (22)
C ₁₀	0.2556 (27)	0.3456 (13)	0.4636 (22)

Table 3. Components of atomic vibration tensors, $U \times 10^3$, in \AA^2 with standard deviations. For Se and S, the expression is $\exp\{-2\tau^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}a^*b^*hk + 2U_{23}b^*c^*kl + 2U_{31}a^*c^*hl]\}$. For the light atoms, the expression $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ was used.

	U_{11} (U)	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
Se	42.06 (1.71)	56.37 (1.00)	54.93 (0.97)	0.70 (1.40)	-7.84 (0.94)	9.93 (1.62)
S ₁	56.01 (4.75)	56.49 (2.50)	54.67 (2.32)	-9.60 (3.23)	-8.20 (2.03)	9.83 (3.95)
S ₂	49.13 (4.69)	76.99 (3.25)	66.85 (2.82)	-11.26 (3.75)	-19.59 (2.54)	13.12 (4.56)
S ₃	64.12 (5.61)	67.99 (2.87)	58.63 (2.49)	-16.15 (3.67)	-10.59 (2.32)	22.80 (4.15)
S ₄	52.29 (4.88)	56.74 (2.63)	76.07 (2.95)	-5.67 (3.32)	-12.55 (2.32)	24.88 (4.56)
O ₁	72.20 (4.30)					
O ₂	70.99 (4.03)					
N ₁	60.41 (4.53)					
N ₂	57.88 (4.28)					
C ₁	52.91 (5.00)					
C ₂	62.73 (5.83)					
C ₃	64.14 (5.65)					
C ₄	77.03 (6.95)					
C ₅	64.51 (5.83)					
C ₆	55.57 (5.07)					
C ₇	63.12 (5.61)					
C ₈	56.23 (5.16)					
C ₉	75.08 (6.47)					
C ₁₀	78.54 (6.55)					

Table 4. Bond lengths and angles in selenium di(morpholyldithiocarbamate); standard deviations in brackets.

Se-S ₁	2.282 (6)	\AA	$\angle S_1-Se-S_2$	70.5 (2) $^\circ$
Se-S ₂	2.782 (5)		$\angle S_1-Se-S_3$	84.6 (2)
Se-S ₃	2.314 (6)		$\angle S_1-Se-S_4$	155.0 (2)
Se-S ₄	2.791 (6)		$\angle S_2-Se-S_3$	155.1 (2)
S ₁ -C ₁	1.75 (2)		$\angle S_2-Se-S_4$	135.0 (2)
S ₂ -C ₁	1.70 (3)		$\angle S_3-Se-S_4$	69.7 (2)
S ₃ -C ₆	1.81 (2)		$\angle Se-S_1-C_1$	93.2 (8)
S ₄ -C ₆	1.63 (2)		$\angle Se-S_2-C_1$	78.2 (6)
C ₁ -N ₁	1.35 (3)		$\angle Se-S_3-C_6$	92.2 (7)
C ₆ -N ₂	1.35 (2)		$\angle Se-S_4-C_6$	80.6 (7)
N ₁ -C ₂	1.51 (4)		$\angle S_1-C_1-S_2$	117.7 (11)
C ₂ -C ₃	1.53 (3)		$\angle S_1-C_1-N_1$	117.4 (18)
C ₃ -O ₁	1.43 (2)		$\angle S_2-C_1-N_1$	124.8 (15)
O ₁ -C ₄	1.43 (4)		$\angle S_3-C_6-S_2$	117.5 (10)
C ₄ -C ₅	1.51 (3)		$\angle S_3-C_6-N_2$	114.3 (17)
C ₅ -N ₁	1.50 (2)		$\angle S_4-C_6-N_2$	128.2 (17)
N ₂ -C ₇	1.47 (3)		$\angle C_1-N_1-C_6$	122.5 (16)
C ₇ -C ₈	1.58 (3)		$\angle C_1-N_1-C_5$	119.7 (19)
C ₈ -O ₂	1.45 (3)		$\angle C_2-N_1-C_5$	114.0 (17)
O ₂ -C ₉	1.47 (3)		$\angle N_1-C_2-C_3$	108.9 (17)
C ₉ -C ₁₀	1.57 (3)		$\angle C_2-C_3-O_1$	107.8 (15)
C ₁₀ -N ₂	1.57 (3)		$\angle C_3-O_1-C_4$	113.2 (17)
			$\angle O_1-C_4-C_5$	111.3 (19)
			$\angle C_4-C_5-N_1$	108.3 (17)
			$\angle C_6-N_2-C_7$	120.7 (19)
			$\angle C_6-N_2-C_{10}$	123.7 (17)
			$\angle C_7-N_2-C_{10}$	115.7 (15)
			$\angle N_2-C_7-C_8$	104.9 (14)
			$\angle C_7-C_8-O_2$	107.6 (18)
			$\angle C_8-O_2-C_9$	112.6 (14)
			$\angle O_2-C_9-C_{10}$	110.9 (16)
			$\angle C_9-C_{10}-N_2$	102.2 (20)

Table 5. Intermolecular distances.

Se—C ₁₀	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$	3.70 Å
S ₂ —C ₁₀	»	3.84
C ₅ —C ₂	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$	3.91
C ₈ —C ₃	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, $3/2+z$	3.74
C ₈ —O ₁	»	3.52
S ₁ —C ₉	$\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$	3.95
S ₂ —C ₉	»	3.82
C ₁ —C ₉	»	3.61
C ₁ —O ₃	»	3.43
S ₁ —C ₇	x , $-y$, $-1+z$	3.79
C ₁ —C ₇	»	3.73
S ₂ —C ₄	$-x$, $-y$, $-1-z$	3.69
S ₁ —S ₄	$\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$	3.60
S ₁ —C ₈	»	3.71
S ₁ —C ₇	»	3.96
C ₉ —C ₄	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$	3.74
C ₉ —O ₁	»	3.83
Se—S ₂	$-x$, $-y$, $-z$	3.89
S ₄ —C ₅	»	3.69
C ₄ —C ₂	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$	3.36
O ₃ —C ₅	»	3.61
O ₃ —N ₁	»	3.31
S ₄ —C ₁	x , y , $1+z$	3.99
C ₉ —C ₈	$-x$, $1-y$, $1-z$	3.67
C ₉ —C ₈	»	3.82
C ₈ —O ₃	»	3.53
C ₂ —O ₁	$1-x$, $-y$, $-1-z$	3.42
C ₃ —O ₁	»	3.44
O ₁ —O ₁	»	3.43

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

Some intramolecular distances

S ₁ —S ₂	3.093 (5) Å
S ₁ —S ₃	2.952 (5)
S ₃ —S ₄	2.944 (5)

selenium and sulfur were corrected for anomalous dispersion according to Cromer¹² using f' and f'' values from *International Tables*. Final observed and calculated structure factors are listed in Table 1. The corresponding positional and thermal parameters are listed in Tables 2 and 3, respectively. Interatomic distances and angles are shown in Tables 4 and 5.

DESCRIPTION OF THE STRUCTURE

The crystals consist of separate molecules of selenium di(morpholyldithiocarbamate) as shown in Fig. 1. The shape of the molecule closely resembles that of the isomorphous tellurium compound.⁸ As seen from Fig. 2, the configuration around the central atom is essentially the same as that found in tellurium di(ethylxanthate),⁵ tellurium di(morpholyldithiocarbamate),⁸ and selenium bis(diethylthiocarbamate).⁹ All atoms of the SeS₄ group are within

0.055 Å of the least squares plane through that group. Thus, selenium di(morpholyldithiocarbamate) may be considered a distorted square planar complex of divalent selenium.

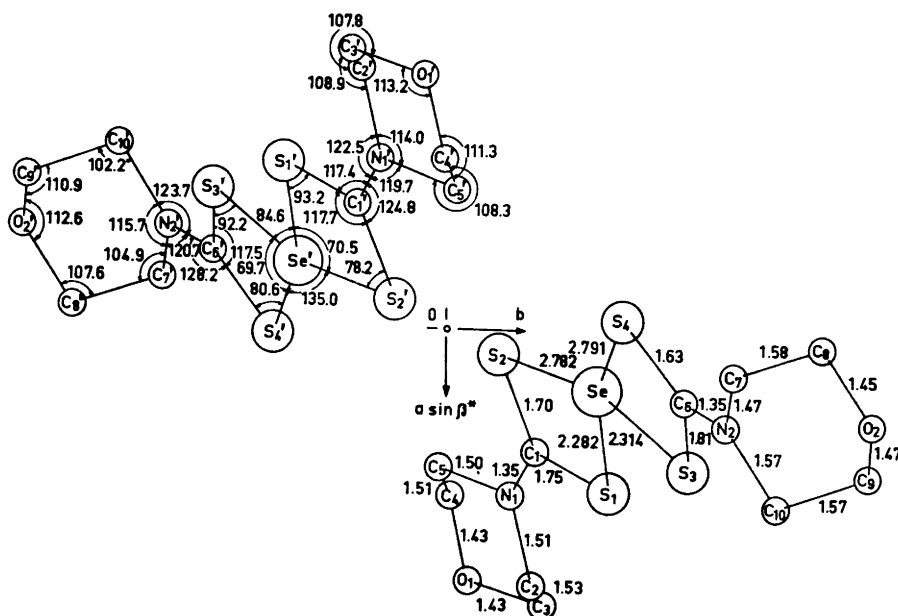


Fig. 1. A pair of selenium di(morpholyldithiocarbamate) molecules related by a center of symmetry seen in the projection along the c axis.

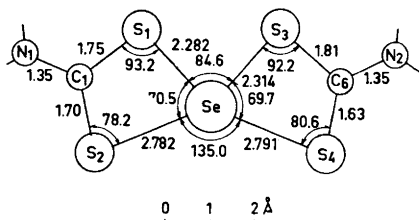


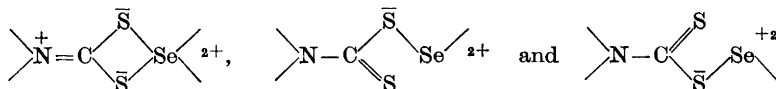
Fig. 2. The configuration around the central selenium atom as seen along the normal to the least squares plane through the nearly planar SeS_4 group.

In each molecule, the four ligand sulphur atoms are bonded to selenium. There is one short and one long Se-S bond from each of the two ligands, with bond lengths $\text{Se-S}_1 = 2.282(6)$ Å, $\text{Se-S}_2 = 2.782(5)$ Å, $\text{Se-S}_3 = 2.314(6)$ Å, and $\text{Se-S}_4 = 2.791(6)$ Å. The corresponding bond angles are $\text{S}_1\text{-Se-S}_2 = 70.5(2)^\circ$, $\text{S}_1\text{-Se-S}_3 = 84.6(2)^\circ$, $\text{S}_3\text{-Se-S}_4 = 69.7(2)^\circ$ and $\text{S}_2\text{-Se-S}_4 = 135.0(2)^\circ$. These bond lengths and angles agree well with those found in selenium bis(diethyldithiocarbamate),⁹ but the two intraligand angles $\text{S}_1\text{-Se-S}_3$ and $\text{S}_2\text{-Se-S}_4$ differ significantly in the two compounds, their

values being 87.7 and 131.5°, respectively, in the latter. This may be due to the closer intermolecular approach of two molecules of selenium di(morpholyldithiocarbamate) across a center of symmetry, as evidenced by the intermolecular, near van der Waals $\text{Se} \cdots \text{S}_2$ contact of 3.893(5) Å. This is illustrated in Fig. 1, which shows such a pair of molecules related by a center of symmetry. As a consequence, the angle $\text{S}_2 - \text{Se} - \text{S}_4$ increases relative to the corresponding angle in selenium bis(diethylthiocarbamate),⁹ where there are no such close contacts. As the intraligand angles are constant, the angle $\text{S}_1 - \text{Se} - \text{S}_3$ must decrease if the SeS_4 group is to remain planar.

The two three-center systems $\text{S}_1 - \text{Se} - \text{S}_4$ and $\text{S}_2 - \text{Se} - \text{S}_3$, both deviating about 25° from linearity, have an average length of 5.085 Å. This value may be compared to 5.072 Å, the corresponding value found in selenium bis(diethylthiocarbamate).⁹ Assuming covalent radii for the sulfur atoms in such a system, these values correspond to selenium radii of 1.503 and 1.496 Å, respectively. These values agree well with 1.49 Å, the radius of the central selenium atom found in the linear three-center system in the triselenocyanate ion.¹³⁻¹⁵

There are, as usual, two different C-S bond lengths in each ligand, the two pairs being $\text{C}_1 - \text{S}_1 = 1.75(2)$ Å, $\text{C}_1 - \text{S}_2 = 1.70(2)$ Å, and $\text{C}_6 - \text{S}_3 = 1.81(2)$ Å, $\text{C}_6 - \text{S}_4 = 1.63(2)$ Å. To each short C-S bond, there corresponds a long S-Se bond and *vice versa*. Compared to the C-S single bond length of 1.81 Å, three of the C-S bonds are shorter than a single bond, though $\text{C}_1 - \text{S}_1$ is not significantly so. As found in other dithiocarbamates,^{8,9} the $\text{N}-\text{C}$ bond lengths are significantly shorter than the sum of the respective covalent single-bond radii, 1.47 Å, both being 1.35 Å. As in isomorphous tellurium di(morpholyldithiocarbamate),⁸ the molecules are roughly planar except for hydrogen and the outer halves of the morpholyl groups. The least squares plane through the molecule, excluding these outer halves, is within 0.36 Å of the thirteen atoms defining it. Thus, the molecule is less planar than selenium bis(diethylthiocarbamate),⁹ where the corresponding distance is only 0.12 Å. The greater deviation from planarity in the present case is probably due to packing effects caused by the bulky morpholyl groups.⁸ Angles on the C and N atoms involved in partial double bonding correspond to sp^2 hybridization of these atoms. On the basis of the above, we assume that as in the analogous compounds,^{8,9} resonance forms of the type



contribute to the structure, the last form being much less important than the others.

Bond lengths and angles in the two morpholyl groups correspond to normal values within the error limits, and both rings have the chair form.

The packing of the molecules is similar to that of the isomorphous tellurium compound.⁸ Intermolecular distances are listed in Table 5; for illustrations, reference may be made to the article on the tellurium isomorph.⁸

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