

## The Crystal Structure of Tellurium(IV) Catecholate, $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$

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The positions of the oxygen and carbon atoms in the structure of tellurium(IV) catecholate,  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ , have been determined. Tellurium(IV) catecholate forms monoclinic crystals with the cell dimensions  $a = 22.67_8$  Å,  $b = 6.935_8$  Å,  $c = 16.527_4$  Å, and  $\beta = 123.15_4^\circ$ , belonging to the space group  $C2/c$ .

The structure was solved by means of three-dimensional electron density calculations and refined by least squares methods, using 780 independent reflexions, a final  $R$  value of 0.105 being obtained.

Tellurium is four-fold co-ordinated by oxygen, all four oxygen atoms lying on the same side of the tellurium atom. The four Te—O bond distances range from 1.97<sub>7</sub> Å to 2.11<sub>6</sub> Å, the standard deviations being 0.02 Å. There is, in addition, a further oxygen atom situated at a distance of 2.64<sub>4</sub> Å from the tellurium atom on the side opposite to the four Te—O bonds. Since this latter oxygen atom belongs to another  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$  unit, a chainlike structure results.

The crystal structure of tellurium(IV) catecholate,  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ , has been determined in connection with a series of investigations of tellurium compounds containing tellurium-oxygen bonds.

Tellurium(IV) catecholate was studied in 1959 by Antikainen and Lundgren.<sup>1</sup> The space group was found to be  $C2/c$ , and the tellurium atoms were assigned the general position  $8(f)$  with  $x = 0.236$ ,  $y = 0.165$ , and  $z = 0.175$ , by interpreting the Patterson projections  $P(upw)$  and  $P(uvp)$ , and the generalized Patterson function  $P_1(uw)$ . These results were taken to be the starting point of the present investigation.

### [EXPERIMENTAL

Crystals of tellurium(IV) catecholate were prepared according to Antikainen and Mälkönen.<sup>2</sup> Yellow needles were obtained, the majority of which were twinned, but it was possible to pick out a few single crystals suitable for X-ray work with Weissenberg methods. The crystal used in the investigation was a needle of length 0.3 mm ( $b$  axis direction) and cross-section  $0.03 \times 0.025$  mm. The  $b$  axis was chosen as rotation axis,

Table 1. Guinier powder photograph of  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ .  $\text{CuK}\alpha_1$  radiation.  $\lambda(\text{CuK}\alpha_1) = 1.54050\text{\AA}$ .

$h$ $k$ $l$	$10^6 \sin^2\theta$ obs	$10^6 \sin^2\theta$ calc	$ F  \times 10^{-1}$ calc	$I$ obs
2 0 0	659	658	52	vvs
2 0 -2	911	910	34	vs
0 0 2	1243	1240	16	w
1 1 0	1399	1398	21	vw
1 1 -1	1458	1461	25	s
4 0 -2	1896	1897	27	m
1 1 1	1953	1955	21	m
1 1 -2	2137	2144	20	s
3 1 -2	2466	2472	8	vvw
4 0 0	2629	2633	25	w
1 1 2	3125	3132	25	s
3 1 -3	3279	3281	28	s
1 1 -3	3444	3447	23	s
4 0 -4	3633	3640	7	
2 0 -4	3633	3641	14	vw
3 1 1	3782	3766	24	m
6 0 -2	4199	4200	54	m
5 1 -3	4428	4432	27	w
0 2 0	4933	4934	22	
1 1 3	4933	4929	32	s
0 0 4	4952	4959	30	w
0 2 1	5235	5244	20	w
5 1 -4	5361	5366	18	
1 1 -4	5361	5369	27	s
2 2 -1	5398	5408	22	w
2 2 0	5583	5592	13	vw
0 2 2	6169	6174	9	vvw
2 2 -2	5842	5844	14	vvw
2 2 1	6397	6396	14	vw
3 1 -5	6763	6758	15	vvw
4 2 -1	6896	6889	22	
5 1 1	6896	6893	16	s
7 1 -3	6896	6899	28	
7 1 -4	7346	7340	14	
1 1 4	7346	7345	13	w
8 0 -4	7583	7587	16	vw
3 1 3	7720	7727	21	w
8 0 -2	7817	7820	42	w
1 1 -5	7898	7911	23	w
6 0 -6	8184	8189	19	vw
7 1 -5	8398	8400	18	vw
4 2 -4	8572	8574	9	
2 2 -4	8572	8575	7	vw
2 0 -6	8847	8852	33	m
5 1 -6	9101	9095	12	vw
3 1 -6	9421	9426	17	w
6 2 -1	9682	9686	27	m
7 1 -6	10085	10080	12	vvw
1 1 5	10374	10382	17	w
0 0 6	11169	11159	40	m
7 1 1	11343	11337	15	vvw
5 1 3	11844	11843	20	vw
6 2 1	12661	12651	14	vvw

Table 1. Continued.

10 0 -2	12757	12756	29	vw
1 3 2	12996	13000	30	m
2 2 -6	13776	13786	12	
8 2 -1	13776	13800	18	vw
6 0 -8	13893	13903	25	vw
5 3 -2	13975	13986	14	vw
3 1 5	14153	14169	11	vw
5 3 -3	14298	14300	8	
5 3 -1	14298	14291	9	vw
8 0 -8	14566	14559	20	
4 0 -8	14566	14564	27	s
3 3 -4	14566	14579	23	
2 0 6	14765	14780	32	w
5 3 -4	15253	15235	23	
1 3 -4	15253	15237	21	s
6 2 -7	15669	15671	18	vw
2 0 -8	16539	16542	29	m
8 2 -7	16795	16820	18	
12 0 -4	16795	16800	20	w
7 3 -4	17228	17208	25	
1 3 4	17228	17214	17	m
5 3 2	18933	18926	19	w
3 3 -6	19307	19294	15	w
0 4 0	19724	19737	9	
2 2 6	19724	19715	11	vw
4 0 6	19724	19719	21	
0 4 1	20059	20047	19	w
2 4 -1	20194	20211	21	w
9 3 -4	20497	20498	19	
3 3 4	20497	20506	18	w
2 4 1	21199	21199	17	vw
4 4 -1	21671	21692	20	vw
11 3 -4	25103	25105	17	
5 3 4	25103	25116	15	w

and Weissenberg photographs of the layers  $h0l-h4l$  were registered. Multiple film techniques employing six films for each layer line were used, giving a ratio between the strongest and the weakest measurable intensities of approximately 2200:1.

In order to determine accurate cell dimensions a Guinier powder photograph was taken, using KCl as internal standard ( $\text{CuK}\alpha_1$  radiation,  $\lambda = 1.54050 \text{ \AA}$ ,  $a_{\text{KCl}} = 6.2919_4 \text{ \AA}$  at  $20^\circ\text{C}^3$ ). 88 lines on the photograph were indexed with the aid of the Algol programme POWDER<sup>4</sup> and a list of observed and calculated  $\sin^2\theta$  values are shown in Table 1. Using the same programme, a least squares refinement based on these lines gave the following cell dimensions:

$$\begin{aligned}
 a &= 22.678 \pm 0.003 \text{ \AA} \\
 b &= 6.9355 \pm 0.0008 \text{ \AA} \\
 c &= 16.5274 \pm 0.0015 \text{ \AA} \\
 \beta &= 123.154^\circ \pm 0.005^\circ \\
 V &= 2176 \text{ \AA}^3.
 \end{aligned}$$

#### DATA PROCESSING

The intensities were estimated visually using an intensity scale prepared by making timed exposures of a chosen reflexion of the actual crystal. The

reflexions of the different film layers were scaled together manually, applying a simple weighting scheme based on the reliability of the estimations within different intervals of degrees of blackness of the intensity scale.

Errors in the intensity material due to absorption effects could not be neglected since the calculated value of the linear absorption coefficient for  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$  was  $232 \text{ cm}^{-1}$ .<sup>5</sup> The absorption correction was performed using a programme written by Abrahamsson<sup>6</sup> for the SAAB D21 computer.

Lorenz' and polarization factors were calculated on the same computer with the programme DR written by Abrahamsson and Larsson.<sup>6</sup>

The  $F_c$  values were brought on to an absolute scale by comparison with  $F_c$  only after an approximate structure had been devised.

#### POSITIONS OF THE LIGHT ATOMS

To obtain maximal resolution in the electron density calculations, the structural parameters of tellurium were refined using the least squares, block diagonal approximation programme written by Wengelin<sup>7</sup> for the SAAB D21 computer. The refinement was based on all 780 observed reflexions, and after five cycles, the  $R$  value dropped to 0.25, and the following parameters were obtained for the tellurium atoms: 8 Te in  $C2/c:8(f)$  with  $x = 0.238$ ,  $y = 0.168$ ,  $z = 0.176$ , and  $B = 4.3 \text{ \AA}^2$ .

A three-dimensional difference Fourier synthesis, based on the signs obtained from the tellurium parameters, was calculated using the Fourier programme written by Larsson.<sup>6</sup> The positions of all oxygen and carbon atoms in the structure were then apparent, the oxygen atoms occupying four of the general positions  $C2/c:8(f)$  and the carbon atoms twelve positions  $C2/c:8(f)$ .

An electron density projection of the structure on the  $xz$  plane is shown in Fig. 1.

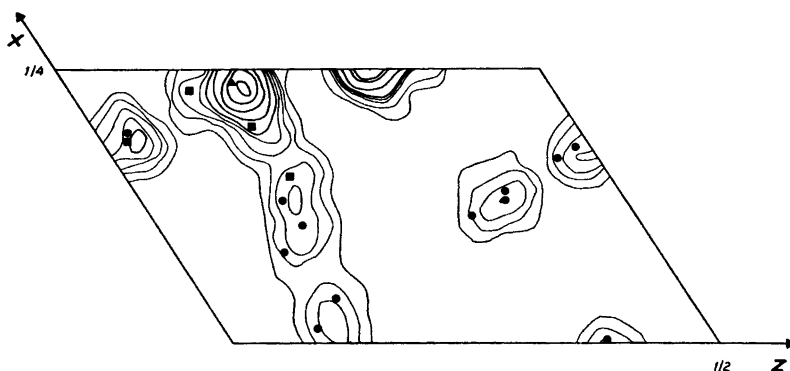


Fig. 1. Electron density projection  $\rho(xpz)$  of  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ . The distance between two thin contours or between one thin and one thick contour within the maxima corresponds to 1/10 of that between two thick contours. The final positions of Te (▲), O (■), and C (●) are indicated.

## REFINEMENT OF THE STRUCTURE

The atomic co-ordinates, isotropic temperature factors, and separate scale factors for each layer line were refined, using the least squares, full matrix programme LALS, modified for the CD 3600 computer in Uppsala.<sup>8</sup> Atomic scattering values given by Cromer and Waber<sup>9</sup> were used, and each structure factor was weighted according to the weighting function devised by Cruickshank ( $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ ) with  $a = 30$ ,  $c = 0.004$ , and  $d = 0$ .

Table 2. Atomic co-ordinates, expressed as fractions of the cell edges, and isotropic thermal parameters in Å<sup>2</sup> for Te(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Te	0.2389 ± 0.0001	0.1688 ± 0.0003	0.1762 ± 0.0001	4.13 ± 0.06
O <sub>1</sub>	0.2333 ± 0.0012	0.4414 ± 0.0041	0.1315 ± 0.0018	5.79 ± 0.52
O <sub>2</sub>	0.1890 ± 0.0010	0.1218 ± 0.0035	0.0353 ± 0.0013	4.26 ± 0.42
O <sub>3</sub>	0.1564 ± 0.0011	0.2406 ± 0.0033	0.1807 ± 0.0014	4.66 ± 0.46
O <sub>4</sub>	0.3011 ± 0.0010	0.3899 ± 0.0033	0.3319 ± 0.0013	4.24 ± 0.43
C <sub>1</sub>	0.3283 ± 0.0013	0.2076 ± 0.0054	0.0184 ± 0.0018	3.73 ± 0.52
C <sub>2</sub>	0.3655 ± 0.0017	0.2068 ± 0.0064	0.1168 ± 0.0023	5.48 ± 0.73
C <sub>3</sub>	0.3813 ± 0.0017	0.0349 ± 0.0068	0.1630 ± 0.0024	5.51 ± 0.75
C <sub>4</sub>	0.1424 ± 0.0021	0.3555 ± 0.0074	0.3874 ± 0.0028	7.17 ± 0.95
C <sub>5</sub>	0.1812 ± 0.0019	0.3583 ± 0.0065	0.4873 ± 0.0025	5.74 ± 0.76
C <sub>6</sub>	0.1948 ± 0.0013	0.4674 ± 0.0054	0.0351 ± 0.0018	3.58 ± 0.56
C <sub>7</sub>	0.1095 ± 0.0015	0.0949 ± 0.0056	0.1553 ± 0.0021	4.56 ± 0.67
C <sub>8</sub>	0.0439 ± 0.0017	0.1333 ± 0.0059	0.1406 ± 0.0023	5.36 ± 0.73
C <sub>9</sub>	0.4984 ± 0.0019	0.4689 ± 0.0069	0.1135 ± 0.0024	5.97 ± 0.80
C <sub>10</sub>	0.4826 ± 0.0017	0.2928 ± 0.0062	0.3959 ± 0.0023	5.46 ± 0.72
C <sub>11</sub>	0.4145 ± 0.0017	0.2536 ± 0.0054	0.3817 ± 0.0022	4.76 ± 0.68
C <sub>12</sub>	0.3686 ± 0.0015	0.4103 ± 0.0051	0.3507 ± 0.0019	3.89 ± 0.59

After four cycles of refinement all parameter shifts became smaller than 5 % of the standard deviations and the *R* value converged to 0.105. The positional co-ordinates and the isotropic temperature factors are given, together with their standard deviations, in Table 2. A comparison between the observed and calculated structure factors is shown in Table 3.

The results of the refinement were supported by the appearance of a three-dimensional  $F_o - F_c$  Fourier synthesis, in which no peak denser than 3.3 electrons/Å<sup>3</sup> could be detected, the  $F_c$  values being obtained from the parameters of Table 2. The highest peaks in the difference maps occurred in the neighbourhood of the tellurium atoms, and were probably due to diffraction effects not accounted for.

Peaks corresponding to some of the hydrogen atoms attached to the benzene rings could be identified in the final difference Fourier maps. These were not, however, included in the refinement, since it was considered, that the contribution to the structure factors due to the hydrogen atoms could give no significant results in a structure containing such a heavy atom as tellurium, and since only reflexions from one axis were used in the calculations.

Table 3. Calculated and observed structure factors for  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$  (The columns are  $l$ ,  $F_o$ , and  $F_c$ , respectively).

0 0 1	6	59	64	9	143	151	-7	52	67	25 1 1	-6	90	91	-16	51	-44	2	214	191				
2 194	-153	14 0 1	11	78	-73	-6	77	-208	-19	25	-27	-5	87	-99	-15	73	-76	4	189	-152			
4 460	-309	-20	32	22	17	29	-29	-4	91	-107	-13	47	-55	-2	115	-109	10	68	-78	10	95	-74	
6 114	-110	-16	65	-74	3 1 1	-3	221	220	-7	55	-64	-1	265	-272	-9	113	-152						
8 175	72	-12	38	39	0	2	57	59	-2	52	59	0	69	77	-8	52	59	7	3 1				
10 101	-93	-10	104	-114	-17	49	44	0	71	74	1	25	31	1	164	145	-7	76	78				
12 26	-8	-8	92	104	-13	63	-62	1	145	-141	5	158	-156	4	68	-59	-5	77	67	-18	47	41	
14 201	-93	-6	150	-143	-12	98	-79	3	211	189	6	42	34	2	113	-122	-3	113	-122	-14	36	-44	
-16 30	-32	-4	156	-183	-11	108	97	0	56	42	-15	34	-40	7	98	86	-2	46	51	-10	39	-137	
-18 140	92	0	91	-92	-9	80	-78	8	72	-69	-13	37	38	8	46	-44	-1	77	79	-6	102	119	
-20 97	-94	-2	166	155	-10	154	123	4	44	47	-7	44	45	13	51	-50	3	62	-65	-5	39	37	
-22 300	293	2	58	-63	-8	52	42	9	62	60	27 1 1			5	42	39				-4	212	-255	
-24 415	-335	4	64	75	-7	44	-41	-5	199	-173				8 2 1									
-26 167	-142	6	45	-51	-6	135	148	11 1 1						18 2 1									
-28 406	335	16 0 1	-4	88	92	-19	51	-48	-15	26	32	-15	81	-73									
0 627	-515	-16	49	52	-3	277	-280	-17	50	45	0 2 1			-13	89	87	-17	47	-53	0	157	149	
2 26	-8	-10	81	98	-1	84	82	-13	91	-95	1	204	-206	-9	164	-170	-11	82	-93	2	154	-136	
4 109	106	-8	82	-96	-1	64	71	-12	98	-106	2	83	87	-8	121	122	-10	59	69	4	123	104	
6 409	-316	-6	54	71	0	56	42	-11	142	155	3	68	65	-7	175	180	-9	88	101	8	65	-61	
8 105	106	-6	54	71	1	247	241	-10	34	43	4	39	30	-5	49	-54	-3	62	65	10	70	63	
10 36	37	-4	108	124	2	94	80	-9	44	-49	5	105	104	-3	156	-157							
12 66	-67	0	70	-76	3	247	-209	-8	57	70	6	71	-95	-2	76	82	20 2 1						
14 68	66	2	45	54	5	129	113	-6	129	-145	7	224	-199	-1	189	181							
-16 65	61	4	67	-69	7	51	54	-3	241	268	8	87	74	0	75	-72	-17	49	47	-14	50	45	
-18 98	-94	18 0 1	8	64	65	8	64	65	-1	55	-61	9	68	56	1	103	-107	-11	50	61	-10	100	105
-20 56	53	-16	52	-65	10	52	-51	1	182	176	14	53	40	5	131	127	-9	44	-60	-5	46	-50	
-22 112	112	-14	41	-26	11	76	73	3	115	-116	15	42	34	13	32	-32							
-24 316	-270	-12	40	59	15	34	-36	7	50	49	2 2 1												
-26 45	50	-10	78	-85	5 1 1									10 2 1									
-28 276	-272	-8	76	-82	-19	25	21	-13	1 1 1		-15	59	48	-17	51	-36							
0 272	249	-4	66	-74	-18	34	29	-19	54	49	-14	46	-32	-15	82	75	24 2 1						
2 54	50	-2	77	85	-17	45	-36	-13	85	95	-12	56	45	-14	91	-85							
4 171	-157	2	76	-42	-12	69	65	-12	74	82	-10	60	56	-13	65	-71	-17	32	35				
6 247	215	4	48	47	-11	94	-92	-11	120	-135	-9	100	93	-9	132	125	-3	33	-34				
8 63	-59	20 0 1	-10	94	-86	-9	94	-86	-7	107	128	-8	100	-90	-8	128	-136	1 3 1					
10 64	60	-16	46	56	-8	35	-27	-6	82	101	-2	185	-172	-7	127	-134							
12 56	-46	-14	37	-44	-7	28	39	-5	226	-242	5	60	54	-6	41	46	-16	46	41	-7	37	42	
-16 90	-77	-8	89	-115	-6	118	112	-5	48	49	-4	76	71	-3	154	152	-12	93	-77	-6	153	168	
-18 70	66	-2	82	-85	-1	190	-184	-1	67	75	-3	34	33	-1	152	-150	-11	49	-8	-4	160	-169	
-20 274	253	-2	82	-80	-3	256	274	3	86	87	-2	119	-159	0	131	124	-10	125	112	0	104	107	
-22 205	-194	2	32	35	-2	45	-41	7	58	-54	-1	158	-226	4	58	-45	-8	94	-91	-2	151	-123	
-24 60	66	4	30	-35	-2	45	-41	7	58	-54	0	136	132	1	96	97	-6	120	-112	4	59	55	
-26 626	542	0	97	82	0	97	82	0	97	82	1	131	137	3	55	56	-5	48	55	8	64	-47	
0 140	-134	22 0 1	1	175	-160	2	89	-82	15 1 1		2	82	-77	5	117	-106	-4	209	212	10	31	32	
2 188	165	-16	43	-51	3	229	198	-19	45	-40	3	58	-48	6	80	77	-2	249	-255				
4 154	-140	-10	66	-75	4	61	57	-13	90	-103	4	75	-74	6	74	58	3	88	-83	13 3 1			
6 46	42	-8	78	99	5	76	-77	-12	40	-49	6	135	113	11	38	-33	4	207	-172				
8 72	64	-4	64	-68	8	42	-48	-8	42	-48	7	169	144	8	92	-83	6	47	46	-10	43	-49	
10 32	-26	2	24	-29	9	91	87	-7	89	-104	8	92	-83	9	76	-62	10	133	125	-6	130	-146	
12 77	73	24 0 1	10	66	57	10	66	57	-5	140	154	12	50	-46	-17	43	44	10	85	-71	-4	99	104
-14 93	-90	-16	43	52	11	53	-50	-5	140	154	12	50	-46	-15	82	-76	12	12	12	8	111	-68	
-16 153	151	-12	50	-55	15	26	26	-3	43	-47	15	37	-30	-13	46	55	16	28	-29	2	111	102	
-18 209	-209	-10	57	62	7 1 1									-11	59	66							
-20 180	-163	-4	40	46	-17	50	53	2	51	53	4 2 1			-10	68	-72	-16	82	-45	15 3 1			
-22 443	-420	-2	38	-43	-15	49	-48	3	45	-51	-15	62	-53	-9	145	-146	-12	90	78	-14	56	-51	
0 261	230	-12	33	39	-13	73	-71	7	41	41	-13	56	54	-7	106	122	-11	55	-48	-12	80	88	
2 50	-55	-11	152	143	8	26	27	-8	26	27	-12	75	-65	-4	70	-70	-10	172	-152	-6	120	130	
4 226	-203	-10	49	-35	-9	102	101	9	18	-24	-9	94	-90	-5	163	-187	-6	155	154	0	100	-111	
6 102	108	-8	29	25	-9	121	-125	8	29	25	-8	134	112	-2	77	77	-5	74	-81	2	86	-81	
8 55	53	-4	37	-41	-7	45	-53	17 1 1						-7	156	156	0	93	-92	-4	220	-234	
-10 101	-93	28 0 1	-6	117	-116	-19	38	42	-6	87	-94	0	85	-77	1	153	-157	-2	120	150	17 3 1		
-12 63	-70	-10	33	45	-5	172	181	-11	47	-59	4	88	-90	3	53	-65	0	61	57	-14	58	58	
-14 94	95	1 1 1	-4	133	145	-4	133	145	-2	68	80	4	56	48	1	42	-43	1	42	-43	-12	73	-94
-16 124	-132	-17	42	-32	0	47	-48	-1	73	78	0	85	-77	7	56	-47	3	69	68	-6	100	-109	
-18 209	226	-15	38	36	1	149	150	1	65	-70	2	153	-157	2	123	108	4	207	180	-4	56	52	
-20 62	-75	-12	44	40	2	124	115	-19 1 1						3	82	72	-17	43	-41	6	43	-46	
-22 288	295	-11	114	-117	3	192	-176	-14	53	44	4	85	81	-16	55	51	8	136	-126	6	22	-21	
0 130	-132	4	101	-92	4	101	-92	4	101	-92	5	144	134	-15	75	72	10	93	77				
2 141	139	-10	122	-103	5	51	48	-13	68	-83	6	119	-102	-11	63	-71	12	43	-36				
4 6	-87	-8	103	99	7	51	53	-12	45	-42	7	153	-137	-10	67	70							
6 132	-127	-7	43	41	8	53	59	-8	47	56	8	76	72	-9	115	131							
-8 62	-75	-6	93	74	9	52	-68	-7	87	-107	9	46	38	-8	58	61	-18	38	-31	-12	56	57	
10 44	-39	-5	254	-230	10	50	-44	-5	46	51	11	43	45	-7	86	-99	-16	25	42	0	65	58	
-12 26	-28	-4																					

Table 3. Continued.

23 3 1	2 4 1	4 4 1	6 4 1	8 4 1	10 4 1	-9 87 95	-3 75 76
-14 50 -58	-15 40 -35	-15 48 46	-15 57 -50	-15 58 58	-15 50 -46	-7 89 -99	-1 69 -57
-8 44 -48	-14 47 -40	-13 62 -49	-13 53 41	-10 66 -57	-13 53 47	-3 109 116	3 54 45
-6 53 55	-15 66 59	-9 90 80	-9 102 -97	-9 86 88	-10 51 45	-1 103 -106	5 32 -27
	-9 80 -71	-8 96 79	-8 91 -81	-8 74 66	-9 94 -106	3 51 -43	
	-8 93 -80	-7 147 -141	-7 108 115	-7 91 -98	-8 43 -38	5 41 35	18 4 1
25 3 1	-7 147 142	-6 76 -72	-6 46 47	-5 41 47	-7 105 119		-9 69 -70
-14 39 39	-6 65 63	-5 80 92	-5 45 -53	-4 35 -46	-3 101 -106	14 4 1	-3 74 -67
-8 40 43	-5 93 -89	-3 77 91	-3 74 -88	-3 81 89	-2 70 -75	-11 53 48	-1 49 42
-6 41 -37	-3 49 -55	-2 68 90	-2 89 -101	-2 84 88	-1 121 139	-9 76 -87	3 32 -33
	-2 56 -65	-1 158 -202	-1 140 164	-1 142 -159	1 49 -47	-7 61 62	
0 4 1	-1 146 205	0 81 -87	0 71 69	1 53 53	3 52 -51	-3 95 -95	20 4 1
1 193 190	0 97 121	1 116 117	1 84 -77	3 52 40	4 53 -56	-1 60 55	-9 64 59
2 42 44	1 167 -165	2 46 34	4 50 -45	4 54 53	5 94 86	3 51 -43	-3 53 50
5 124 -109	3 36 -30	3 41 33	5 113 99	5 97 -90		5 41 35	
6 105 -87	4 45 -45	5 126 -114	6 65 55	6 53 -40			
7 140 128	5 156 121	6 83 -67	7 64 -57		12 4 1		22 4 1
8 56 46	6 71 58	7 93 90	11 40 29		-17 41 -31	16 4 1	
13 57 47	7 119 -109	11 49 -34			-15 50 49	-9 64 64	-9 46 -44
	13 52 -44	13 41 36					-3 38 -36

## SOME GEOMETRICAL CALCULATIONS

The positions of the hydrogen atoms, as calculated by the programme HYDROGENS,<sup>6</sup> assuming  $sp^2$  hybridization of the carbon atoms and C—H bond distances of 1.09 Å in the benzene rings, are given in Table 4.

The best least squares planes through the carbon atoms of the two benzene rings were calculated using the programme PLANEFIT.<sup>7</sup> The deviations of certain atoms from these planes are shown in Table 5.

Table 4. Geometrically calculated positions of the hydrogen atoms in  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ .

	<i>x</i>	<i>y</i>	<i>z</i>
H <sub>2</sub>	0.384	0.341	0.158
H <sub>3</sub>	0.413	0.034	0.241
H <sub>4</sub>	0.129	0.220	0.347
H <sub>5</sub>	0.201	0.224	0.528
H <sub>8</sub>	0.030	0.274	0.157
H <sub>9</sub>	0.445	0.489	0.099
H <sub>10</sub>	0.520	0.174	0.415
H <sub>11</sub>	0.401	0.112	0.395

Table 5. Best least squares planes through the carbon rings (referred to Cartesian co-ordinates in Ångström) and deviations from these planes.

Transformation to Cartesian co-ordinates (*X, Y, Z*):

$$\begin{aligned} X &= 22.678x \\ Y &= 6.9355y \\ Z &= -9.045x + 13.848z \end{aligned}$$

1. Plane through C<sub>1</sub>—C<sub>6</sub>:

$$-0.9976X + 0.0631Y - 0.0268Z = -3.9000 \text{ Å}$$

atom	deviation (Å)	atom	deviation (Å)
C <sub>1</sub>	-0.002	C <sub>6</sub>	0.016
C <sub>2</sub>	-0.015	O <sub>1</sub>	-0.029
C <sub>3</sub>	0.017	O <sub>2</sub>	-0.002
C <sub>4</sub>	-0.003	Te	0.112
C <sub>5</sub>	-0.014		

2. Plane through C<sub>7</sub>-C<sub>12</sub>:

$$0.1951X + 0.1882Y - 0.9626Z = -1.7558 \text{ \AA}$$

atom	deviation (Å)	atom	deviation (Å)
C <sub>7</sub>	0.018	C <sub>12</sub>	-0.033
C <sub>8</sub>	0.001	O <sub>3</sub>	0.032
C <sub>9</sub>	-0.005	O <sub>4</sub>	-0.048
C <sub>10</sub>	-0.009	Te	0.370
C <sub>11</sub>	0.028		

Angle between the planes: 99.03°

Table 6. Distances and angles in the tellurium-oxygen co-ordination polyhedron. (Standard deviations in parentheses).

Te-O <sub>1</sub>	2.008(28) Å	O <sub>1</sub> -O <sub>3</sub>	3.442(34) Å
Te-O <sub>2</sub>	1.981(19)	O <sub>1</sub> -O <sub>4</sub>	3.342(36)
Te-O <sub>3</sub>	1.977(22)	O <sub>2</sub> -O <sub>3</sub>	2.990(28)
Te-O <sub>4</sub>	2.110(23)	O <sub>2</sub> -O <sub>4</sub>	2.630(30)
Te-O <sub>4</sub> '	2.644(21)	Te-Te	4.110(02) (2 ×)
O <sub>1</sub> -Te-O <sub>2</sub>		80.9(1.0)°	
O <sub>1</sub> -Te-O <sub>3</sub>		84.6(0.9)	
O <sub>1</sub> -Te-O <sub>4</sub>		154.3(0.9)	
O <sub>2</sub> -Te-O <sub>3</sub>		98.1(0.8)	
O <sub>2</sub> -Te-O <sub>4</sub>		79.9(0.9)	
O <sub>3</sub> -Te-O <sub>4</sub>		81.4(0.9)	

Table 7. Distances and angles in the catecholate groups. (Standard deviations in parentheses).

O <sub>1</sub> -O <sub>2</sub>	2.588(36) Å	C <sub>1</sub> -C <sub>6</sub> -O <sub>1</sub>	113.6(3.0)°
O <sub>1</sub> -C <sub>6</sub>	1.346(35)	C <sub>5</sub> -C <sub>6</sub> -O <sub>1</sub>	126.6(3.2)
O <sub>2</sub> -C <sub>1</sub>	1.400(41)	C <sub>6</sub> -C <sub>1</sub> -O <sub>2</sub>	116.5(2.2)
C <sub>6</sub> -C <sub>1</sub>	1.423(49)	C <sub>2</sub> -C <sub>1</sub> -O <sub>2</sub>	122.4(3.3)
C <sub>1</sub> -C <sub>2</sub>	1.363(40)	C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub>	121.0(3.4)
C <sub>2</sub> -C <sub>3</sub>	1.354(61)	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	118.5(3.7)
C <sub>3</sub> -C <sub>4</sub>	1.428(65)	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	122.6(3.3)
C <sub>4</sub> -C <sub>5</sub>	1.383(52)	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	118.4(4.1)
C <sub>5</sub> -C <sub>6</sub>	1.383(55)	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	119.5(3.9)
		C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	120.0(2.6)
O <sub>3</sub> -O <sub>4</sub>	2.666(32) Å	C <sub>12</sub> -C <sub>7</sub> -O <sub>3</sub>	117.1(2.7)°
O <sub>3</sub> -C <sub>7</sub>	1.357(42)	C <sub>8</sub> -C <sub>7</sub> -O <sub>3</sub>	119.5(3.3)
O <sub>4</sub> -C <sub>12</sub>	1.392(34)	C <sub>7</sub> -C <sub>12</sub> -O <sub>4</sub>	117.9(2.8)
C <sub>12</sub> -C <sub>7</sub>	1.396(51)	C <sub>11</sub> -C <sub>12</sub> -O <sub>4</sub>	120.8(3.0)
C <sub>7</sub> -C <sub>8</sub>	1.397(45)	C <sub>12</sub> -C <sub>7</sub> -C <sub>8</sub>	123.3(3.3)
C <sub>8</sub> -C <sub>9</sub>	1.436(58)	C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	114.7(3.5)
C <sub>9</sub> -C <sub>10</sub>	1.331(62)	C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>	122.7(3.3)
C <sub>10</sub> -C <sub>11</sub>	1.453(47)	C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	122.4(3.5)
C <sub>11</sub> -C <sub>12</sub>	1.395(48)	C <sub>10</sub> -C <sub>11</sub> -C <sub>12</sub>	115.3(3.2)
		C <sub>11</sub> -C <sub>12</sub> -C <sub>7</sub>	121.2(2.8)

Interatomic distances and angles together with their standard deviations were calculated with the programme DISTAN<sup>8</sup> and are listed in Tables 6 and 7.



## DISCUSSION OF THE STRUCTURE

The basic unit of the structure is formed by the co-ordination of the four oxygen atoms of two catechol groups to one tellurium atom. Apart from van der Waals' forces between the different formula units, the structure may be considered to be held together by a weak intermolecular bond, corresponding to a Te—O distance of 2.644 Å. From this point of view, the structure may be regarded as being composed of rows of  $\text{---O---TeO}_3\text{---O---TeO}_3\text{---O---TeO}_3\text{---}$  running through the structure in the direction of the  $b$  axis, these rows being embedded and isolated from each other by the carbon rings of the catecholate groups.

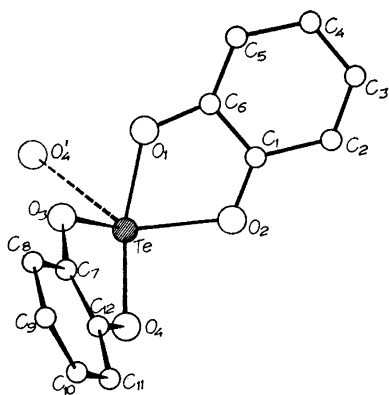


Fig. 2. The formula unit of tellurium(IV) catecholate projected on the (101) plane. (The dotted line shows the intermolecular Te—O<sub>4</sub>' interaction).

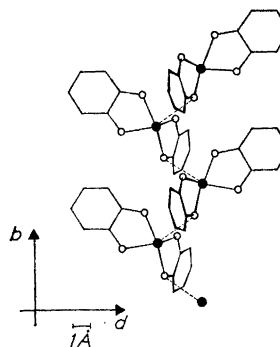


Fig. 3. Part of the structure of  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$ .

A projection of the formula unit on the (101) plane is shown in Fig. 2. In Fig. 3, which shows part of the structure, the short intermolecular Te—O distances are indicated as dotted lines between a few of the molecules in the chain.

Table 8. Comparison of the tellurium-oxygen co-ordination polyhedra in some Te(IV) compounds. (Standard deviations in the distances and angles are approximately 0.02 Å and 0.9°, respectively).

	$\alpha\text{-TeO}_2$	$\beta\text{-TeO}_2$	$\text{Te}_2\text{O}_4\cdot\text{HNO}_3$	$\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$
Te—O (axial)	2.07 Å (2×)	2.07 Å 2.19 Å	2.02 Å 2.16 Å	2.01 Å 2.11 Å
Te—O (equatorial)	1.88 Å (2×)	1.88 Å 1.93 Å	1.88 Å 1.95 Å	1.98 Å 1.98 Å
O <sub>ax</sub> —Te—O <sub>ax</sub>	168.0°	168.9°	147.8°	154.3°
O <sub>eq</sub> —Te—O <sub>eq</sub>	100.6°	101.0°	100.0°	98.1°

The co-ordination of tellurium can be described in terms of a distorted trigonal bipyramid, in which one of the equatorial positions is unoccupied (*cf.* Fig. 2 and Table 6). This type of Te(IV) co-ordination has also been found in  $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$ ,<sup>10</sup>  $\alpha\text{-TeO}_2$ ,<sup>11</sup> and  $\beta\text{-TeO}_2$ ,<sup>12</sup> and a comparison of bond distances and angles is given in Table 8. This co-ordination might be explained, as suggested by Pauling<sup>13</sup> and also pointed out by Beyer *et al.*,<sup>12</sup> in terms of a  $5s5p^35d$  hybrid with an unshared electron pair occupying one of its equatorial orbitals. Swink and Carpenter<sup>10</sup> have considered the equatorial bonds to be formed from the  $5s$ ,  $5p_x$ , and  $5p_y$  orbitals and the axial bonds from the  $5p_z$  and  $6s$  orbitals of the tellurium atom.

There is, however, no need to involve the doubtful  $5d$  or  $6s$  orbitals of the tellurium atom in bonding, if the equatorial bonds are considered to arise through the combination of the  $5s$ ,  $5p_x$ , and  $5p_y$  atomic orbitals of tellurium, and if the axial molecular orbitals involve only the  $5p_z$  orbital of the tellurium atom and the  $p_z$  orbitals of  $\text{O}_1$  and  $\text{O}_4$ . Three different axial molecular orbitals are thus possible:

1.  $p_z(\text{Te}) - (p_z(\text{O}_1) + p_z(\text{O}_4))$  — bonding orbital
2.  $p_z(\text{Te}) + (p_z(\text{O}_1) - p_z(\text{O}_4))$  — non-bonding orbital
3.  $p_z(\text{Te}) + (p_z(\text{O}_1) + p_z(\text{O}_4))$  — anti-bonding orbital.

Since there are 10 electrons available to fill the molecular orbitals, and if a lone pair is assumed to exist in the equatorial position, the axial bonds are formed by one bonding and one non-bonding molecular orbital. This model of the electronic configuration is also in accordance with the fact that the axial bonds are weaker than the equatorial bonds (*cf.* Table 8).

In  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$  the  $\text{Te}-\text{O}_1$  bond is not significantly longer than the equatorial bonds. If, however, a weak interaction was assumed to exist between  $\text{O}_4$  and the unshared electron pair of the tellurium atom in the neighbouring molecule,  $\text{O}_4$  would not contribute to the axial molecular bond as much as  $\text{O}_1$ .

The effect of lonepair-bond-pair repulsion<sup>14</sup> may be seen in all of the structures cited in Table 8. In  $\text{Te}(\text{C}_6\text{H}_4\text{O}_2)_2$  this distortion is more accentuated than in  $\alpha\text{-TeO}_2$  and  $\beta\text{-TeO}_2$ , and might perhaps be attributed to steric hindrance caused by the fixed O—O distance of approximately 2.6 Å in the catecholate groups.

No significant differences have been found in the bond distances and angles of the catecholate groups (*cf.* Table 7) as compared with those of catechol.<sup>15</sup> The mean C—C bond distance in the carbon ring containing  $\text{C}_1-\text{C}_6$  is 1.389 Å and the mean C—O distance is 1.373 Å, while the corresponding values in the other ring are 1.401 Å and 1.375 Å, respectively. These values are the same within the standard deviations as those found in catechol: 1.385 Å (C—C) and 1.372 Å (C—O).

There are no significant deviations of the carbon atoms from the best least squares plane through the actual rings (*cf.* Table 5). The tellurium atom is situated approximately in the plane defined by one of the catecholate groups, but is at a distance of 0.37 Å from the plane through the catecholate

group containing  $O_4$ . This difference between the two catecholate groups also supports the assumption that there is a weak intermolecular bond between  $O_4$  and Te.

During the course of this investigation, it was pointed out to me that a similar compound,  $K[As(C_6H_4O_2)_2]$ , had recently been solved.<sup>16</sup> In this structure As(III) shows a similar Me—O arrangement to that observed for Te(IV) in  $Te(C_6H_4O_2)_2$ , but the trigonal bipyramid in  $K[As(C_6H_4O_2)_2]$  is slightly less distorted, the angle between the axial bonds being  $166.2^\circ$  and that between the two occupied equatorial bonds being  $101.5^\circ$ . In the arsenic compound there is, in distinction from  $Te(C_6H_4O_2)_2$ , a clear difference between axial and equatorial bond lengths, i.e. 1.997 Å and 1.943 Å (axial) and 1.805 Å and 1.809 Å (equatorial). No intermolecular bond corresponding to that observed in  $Te(C_6H_4O_2)_2$  has, however, been found in  $K[As(C_6H_4O_2)_2]$ .

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#### REFERENCES

1. Antikainen, P. J. and Lundgren, G. *Suomen Kemistilehti* **B 32** (1959) 175.
2. Antikainen, P. J. and Mätkönen, P. J. *Z. anorg. allgem. Chem.* **299** (1959) 292.
3. Hambling, P. *Acta Cryst.* **6** (1953) 98.
4. Lindqvist, O. and Wengelin, F. *To be published.*
5. *International Tables for X-ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1952, Vol. I.
6. Abrahamsson, S., Aleby, S., Larsson, K., Nilsson, B., Selin, K. and Westerdahl, A. *Acta Chem. Scand.* **19** (1965) 758.
7. Wengelin, F. *To be published.*
8. Lundgren, J.-O. and Liminga, R. *Private communication.*
9. Cromer, Don T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
10. Swink, L. N. and Carpenter, G. B. *Acta Cryst.* **21** (1966) 578.
11. Lindqvist, O. *To be published.*
12. Beyer, H., Sahl, K. and Zemann, J. *Naturwiss.* **52** (1965) 155.
13. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, New York 1960, p. 181.
14. Gillespie, R. J. and Nyholm, R. S. *Quart. Rev.* **11** (1957) 339.
15. Brown, C. J. *Acta Cryst.* **21** (1966) 170.
16. Skapski, A. C. *To be published.*

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