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Refinement of the Structure of Tripotassium–Ditungsten–Enneachloride, $K_3W_2Cl_9$

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The structure of $K_3W_2Cl_9$ has been redetermined from single crystal data and found to be in agreement with that given by Brosset (1935). The parameters were refined by Fourier and least-squares methods. The W–W bond in the $W_2Cl_9^{-3}$ complex is of a length corresponding to a double bond.

The structure of $K_3W_2Cl_9$ was established originally by Brosset (1935) on the basis of powder data and has been discussed by Pauling (1947*a*). The present note describes a refinement based on single crystal data.

The symmetry of precession photographs and the systematic extinctions found ($00l$ only when $l \neq 2n$) are compatible with the space group proposed by Brosset (1935), C_{6h}^2–$P6_3/m$. The unit-cell dimensions were determined from back reflections whose Bragg angles were established from fortunate coincidences with diamond powder lines. They are: $a = 7{\cdot}17_1$ Å and $c = 16{\cdot}25_8$ Å, based on Straumanis' and Aka's (1951) value of 3·5668 Å for the cubic lattice constant of diamond. Intensity data were obtained with Mo K radiation from single crystals which had been ground to cylinders of less than 0·1 mm. diameter. The intensities of the $hh0$, $h0l$, and hhl zones were collected on the Weissenberg goniometer using the multiple-film technique and were estimated visually by comparison with a reference scale prepared by varying the exposure time of a selected reflection. The intensities were corrected for absorption (*Internationale Tabellen*, 1935) as well as for Lorentz and polarization factors (Lu, 1943).

The unit cell contains two $K_3W_2Cl_9$ units. Of the six K atoms, two (K_a) occupy positions (a) (*Internationale Tabellen*, 1935) with coordinates $\pm(0, 0, \frac{1}{4})$, while the other four (K_f) are located in set (f), $\pm\{(\frac{1}{3}, \frac{2}{3}, z), \pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)\}$, which has one free parameter z_K. The four W atoms have a similar set of coordinates (f), the parameter assuming the value z_W. Of the eighteen Cl atoms, six (Cl_m) are in set (m), $\pm\{(p, q, \frac{1}{4}); (\bar{q}, p-q, \frac{1}{4}); (q-p, \bar{p}, \frac{1}{4})\}$, while the other twelve (Cl_i) are in the general position (i), $\pm\{[(x,y,0); (\bar{y},x-y,0); (y-x,\bar{x},0)]+[(0,0,z); (0,0,\frac{1}{2}-z)]\}$. There are seven positional parameters.

Brosset's values for these parameters were found in reasonable agreement with our intensity data and the parameters were refined first by the use of Fourier projections in which the W-atoms had been subtracted, and later by seven cycles of least-squares refinements (Hughes, 1941). Two of these refinements were run on an Elecom digital computer, using a program developed by Dr H. Steinfink & Miss E. E. Allen, the remaining five on a Datatron digital computer, using a program written by Lavine & Rollett (1956). Both programs use a weighting scheme proposed by Hughes (1941) and in both programs shifts of the temperature parameters may be computed. Unobserved structure factors are given zero weight in the Elecom program while they are included in the Datatron program, provided the computed values are larger than a minimum value, $F_{\text{min.}}$, chosen close to the values actually observed for the weakest reflections, and for simplicity taken to be constant. In addition, in the computation of F_o-F_c, F_o is taken to be $F_{\text{min.}}$ rather than zero. In the present work $F_{\text{min.}} = 20{\cdot}0$ (or $2{\cdot}5\ F_{\text{min.}} = 50$ in Table 2).

During the refinement the R-factor dropped from 0·215 to 0·131, while the weighted sum of residuals decreased from 30·9 to 11·9. The ratio $\Sigma|F_c|/\Sigma|F_o|$ is 1·011. Table 1 lists the final parameter values together with their variances in fractions of unit-cell edges as well as in Å, as they were obtained from the least-squares treatment. Also listed are the temperature parameters which were employed in the usual expression $\exp(-B\sin^2\theta/\lambda^2)$ in the computation of the structure factors.

Table 1. *Atomic parameters*

Atoms	Parameters	σ	σ (Å)	B
K_a	—	—	—	5·0
K_f	$z_K = 0{\cdot}5718$	0·0011	0·02	5·0
W_f	$z_W = 0{\cdot}3241$	0·0002	0·003	2·6
Cl_m	$p = 0{\cdot}4588$	0·0056	0·04	3·6
	$q = 0{\cdot}4472$	0·0056	0·04	—
Cl_i	$x = 0{\cdot}1348$	0·0038	0·03	5·2
	$y = 0{\cdot}3506$	0·0038	0·03	—
	$z = 0{\cdot}4074$	0·0012	0·02	—

The atomic structure amplitudes used were averages between the values given by Pauling & Sherman (1932) with those of Thomas & Fermi (*Internationale Tabellen*, 1935). The W values were all decreased by 0·15 to correct for anomalous dispersion (James, 1954). The observed and computed structure factors are listed in Table 2.

From the unit-cell dimensions and parameters the distances and angles listed in Table 3 or shown in Fig. 1 were computed.

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Table 2. *Structure factors*

Both computed and observed values of the structure factors have been multiplied by a factor 2·5. Starred entries were included in the least-squares procedure, although unobserved, with 2·5 F_o set equal to 50.

*hk*0

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 1 0	336	−377	5 3 0	118	−135	4 6 0	71	−60
1 1 0	529	627	6 3 0	151	170	5 6 0	0	−26
2 1 0	277	−324	7 3 0	0	−41	6 6 0	85	60
3 1 0	258	−323	8 3 0	0	−44	7 6 0	0	−15
4 1 0	408	396	*9 3 0	50	52	8 6 0	15	−15
5 1 0	76	−53	10 3 0	0	−19	0 7 0	103	−87
6 1 0	79	−113	0 4 0	209	−208	1 7 0	135	163
7 1 0	128	156	1 4 0	350	370	2 7 0	65	−64
8 1 0	128	−72	2 4 0	143	−147	3 7 0	54	−60
9 1 0	51	−50	3 4 0	74	−41	4 7 0	105	102
*10 1 0	50	62	4 4 0	225	225	5 7 0	0	−28
11 1 0	0	−20	5 4 0	63	−58	6 7 0	0	−25
0 2 0	323	−291	6 4 0	54	−50	0 8 0	92	−61
1 2 0	147	−130	7 4 0	92	102	1 8 0	0	−36
2 2 0	896	781	8 4 0	0	−34	2 8 0	86	94
3 2 0	196	−216	9 4 0	0	−15	3 8 0	0	−34
4 2 0	120	−133	0 5 0	115	−121	4 8 0	0	−32
5 2 0	271	305	1 5 0	177	−206	5 8 0	0	47
6 2 0	102	−106	2 5 0	262	316	0 9 0	128	137
7 2 0	0	−40	3 5 0	69	−72	1 9 0	0	−44
8 2 0	91	95	4 5 0	76	−85	2 9 0	0	−32
9 2 0	0	−23	5 5 0	101	108	*3 9 0	50	54
10 2 0	0	−21	*6 5 0	50	−50	4 9 0	0	−21
11 2 0	0	37	7 5 0	0	−34	0 10 0	42	−43
0 3 0	565	580	8 5 0	0	46	1 10 0	79	60
1 3 0	181	−148	0 6 0	290	321	2 10 0	0	−23
2 3 0	206	−198	1 6 0	132	−131	3 10 0	0	−17
3 3 0	264	285	2 6 0	85	−98	0 11 0	0	−21
4 3 0	133	−155	3 6 0	134	162	1 11 0	0	−18

The point group symmetry of the $W_2Cl_9^{3-}$ ion is D_{3h}–$\bar{6}2m$, although the space group only requires D_3–32. The configuration of the Cl-atoms is that of two distorted octahedra which share one face and in which the W-atoms are located centrally, but closer

Table 3. *Some interatomic distances and angles*

(*a*) Distances in one complex ion (see also Fig. 1)

Atoms	Distance Å	(Å)	Number of distances per complex ion (per K^+ in parenthesis)
Cl_i–Cl_i	3·44	0·03	6
Cl_m–Cl_m	3·76	0·04	3
Cl_i–Cl_m	3·29	0·03	12

(*b*) Distances between different ions

Cl_m–Cl_m	3·51	0·04	6
Cl_i–Cl_i	3·80	0·03	12
Cl_i–Cl_i	3·30*	0·03	6
Cl_i–Cl_i	3·73*	0·03	6
W–K_f	4·03	0·02	6 (6)
Cl_i–K_a	3·37	0·02	6 (6)
Cl_i–K_f	3·31	0·03	6 (3)
Cl_i–K_f	3·33	0·03	6 (3)
Cl_i–K_f	3·89	0·03	6 (3)
Cl_m–K_a	3·25	0·02	3 (3)
Cl_m–K_a	3·92	0·02	3 (3)
Cl_m–K_f	3·54	0·03	6 (3)

(*c*) Angles

	Angle	(Degree)
Cl_i–W–Cl_i	91·4°	0·9°
Cl_m–W–Cl_m	98·4	1·0
Cl_i–W–Cl_m	84·8	0·8

* Involving anions in different layers.

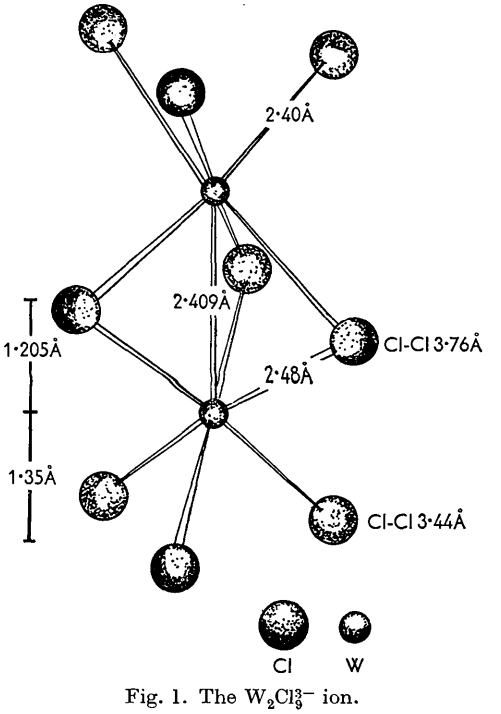

Fig. 1. The $W_2Cl_9^{3-}$ ion.

Table 2 (*cont.*)

hhl

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
1	1	1	0	3	2	2	20	93	−95	4	4	15	0	8
1	1	2	306	−321	2	2	21	0	−1	4	4	16	122	42
1	1	3	195	−177	2	2	22	89	53	4	4	17	0	−5
1	1	4	119	−106	2	2	23	0	1	4	4	18	0	37
1	1	5	0	37	2	2	24	0	24	4	4	19	0	2
1	1	6	406	470	3	3	1	0	10	4	4	20	90	−63
1	1	7	0	15	3	3	2	155	−156	4	4	21	0	−3
1	1	8	406	−437	3	3	3	137	−137	4	4	22	0	30
1	1	9	99	90	3	3	4	62	− 69	5	5	1	0	4
*1	1	10	50	−53	3	3	5	0	37	5	5	2	74	−59
1	1	11	0	−41	3	3	6	255	266	5	5	3	0	−24
1	1	12	221	237	3	3	7	0	7	5	5	4	0	−29
1	1	13	0	−9	3	3	8	229	−240	5	5	5	0	8
1	1	14	216	−208	3	3	9	78	91	5	5	6	95	98
1	1	15	0	−39	3	3	10	0	−16	5	5	7	0	−1
1	1	16	136	126	3	3	11	0	−45	5	5	8	113	−87
1	1	17	0	28	3	3	12	151	132	5	5	9	0	16
1	1	18	122	106	3	3	13	0	−5	5	5	10	0	−1
1	1	19	0	1	3	3	14	153	−126	5	5	11	0	−8
1	1	20	189	−167	3	3	15	0	−42	5	5	12	76	55
1	1	21	0	12	3	3	16	85	69	5	5	13	0	0
*1	1	22	50	61	3	3	17	0	31	*5	5	14	50	−56
1	1	23	0	−12	3	3	18	89	68	6	6	1	0	−4
1	1	24	0	11	3	3	19	0	−0	6	6	2	0	−32
2	2	1	0	−3	3	3	20	136	−105	6	6	3	0	8
2	2	2	262	−265	3	3	21	0	14	6	6	4	0	−16
2	2	3	0	10	3	3	22	0	43	6	6	5	0	−5
2	2	4	152	−121	3	3	23	0	−13	6	6	6	85	53
2	2	5	0	−4	3	3	24	0	7	6	6	7	0	3
2	2	6	131	107	4	4	1	0	−9	6	6	8	0	−47
2	2	7	0	1	4	4	2	123	−104	6	6	9	0	−6
2	2	8	256	−257	4	4	3	0	22	6	6	10	0	1
2	2	9	0	−6	4	4	4	66	−50	7	7	1	0	−0
2	2	10	0	4	4	4	5	0	−11	7	7	2	0	−18
2	2	11	0	3	4	4	6	148	132	7	7	3	0	−0
2	2	12	327	326	4	4	7	0	6	7	7	4	0	−8
2	2	13	0	−1	4	4	8	140	−139	7	7	5	0	−0
2	2	14	242	−252	4	4	9	0	−15	7	7	6	0	26
2	2	15	0	3	4	4	10	0	−1	8	8	1	0	−0
2	2	16	140	85	4	4	11	0	9	8	8	2	0	−8
2	2	17	0	−2	4	4	12	120	109	9	9	1	0	−0
2	2	18	0	38	4	4	13	0	−3	9	9	2	0	−4
2	2	19	0	0	4	4	14	139	−100					

to the plane of the shared face (1·205 Å) than to the planes of the peripheral faces (1·35 Å). The W–W distance of 2·409 Å is shorter than in metallic W (2·519 Å) and corresponds, in fact, closely to the length expected for a W=W double bond (Pauling, 1947*b*). The W–Cl bonds to the shared Cl atoms are longer than those of the peripheral Cl atoms. The two triangles formed by the peripheral Cl atoms, are rotated by 60·0° relative to the triangle of the central Cl atoms, as is normal for two octahedra sharing faces. (A recent description of the $W_2Cl_9^{3-}$ complex (Wessel & IJdo, 1957), according to which the above angle is 37·5°, is erroneous.)

While the W-atoms evidently are joined by a bond, the situation is different in the related $Cr_2Cl_9^{3-}$ complex. As reported in a recent paper by Wessel & IJdo (1957) on the crystal structure of $Cs_3Cr_2Cl_9$ the Cr-atoms are closer to the planes of the peripheral Cl-atoms than to the plane of the shared Cl-atoms, and the magnetic moment of $Cs_3Cr_2Cl_9$ indicates 3 unshared electrons per Cr-atom while the W-complex is diamagnetic.

The centers of the $W_2Cl_9^{3-}$ ions have the parameters of hexagonal closest packing. The ratio of c/a (2·267) to the corresponding quantity (1·633) for hexagonally closest packed spheres is 1·39, which is a measure of the ellipticity of the anions. Either kind of K^+ ion has twelve chlorine neighbors.

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Table 2 (*cont.*)

h0l

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 0 2	368	−454	3 0 3	0	23	5 0 17	0	−10
0 0 4	208	−213	3 0 4	95	−93	5 0 18	0	−43
0 0 6	121	−81	3 0 5	0	25	5 0 19	72	71
0 0 8	270	−316	3 0 6	266	331	5 0 20	74	60
0 0 10	0	22	3 0 7	0	−42	*5 0 21	50	−67
0 0 12	555	513	3 0 8	294	−344	5 0 22	0	−27
0 0 14	345	−369	3 0 9	0	−10	6 0 1	0	23
0 0 16	98	103	3 0 10	0	−37	6 0 2	142	−138
0 0 18	0	20	3 0 11	0	−7	6 0 3	0	4
0 0 20	93	−96	3 0 12	208	237	6 0 4	70	−64
0 0 22	60	65	3 0 13	0	27	6 0 5	0	15
0 0 24	0	37	3 0 14	218	−204	6 0 6	131	145
1 0 1	444	−535	3 0 15	0	−0	6 0 7	0	−22
1 0 2	141	149	3 0 16	125	108	6 0 8	173	−170
1 0 3	77	85	3 0 17	0	1	6 0 9	0	−0
1 0 4	94	87	3 0 18	89	80	6 0 10	0	−2
1 0 5	346	422	3 0 19	0	−11	6 0 11	0	−6
1 0 6	222	−238	3 0 20	136	−136	6 0 12	181	151
1 0 7	317	−368	3 0 21	0	2	6 0 13	0	15
1 0 8	208	240	*3 0 22	50	54	6 0 14	157	−132
1 0 9	181	196	3 0 23	0	−0	6 0 15	0	−2
1 0 10	0	14	3 0 24	0	14	*6 0 16	50	53
1 0 11	95	67	4 0 1	197	−226	6 0 17	0	2
1 0 12	143	−134	4 0 2	0	−13	6 0 18	0	41
1 0 13	301	−317	4 0 3	162	181	7 0 1	117	−123
1 0 14	109	115	4 0 4	170	180	7 0 2	19	5
1 0 15	168	153	4 0 5	232	279	7 0 3	57	53
1 0 16	73	−64	4 0 6	173	−164	7 0 4	83	72
1 0 17	0	47	4 0 7	302	−340	7 0 5	128	123
1 0 18	0	−49	4 0 8	209	217	7 0 6	95	−85
1 0 19	91	−97	4 0 9	42	58	7 0 7	184	−149
1 0 20	93	81	4 0 10	100	−90	7 0 8	117	98
1 0 21	115	115	4 0 11	72	63	7 0 9	44	48
1 0 22	0	−30	4 0 12	89	−75	7 0 10	0	−35
1 0 23	0	−34	4 0 13	139	−161	7 0 11	79	34
1 0 24	0	−8	*4 0 14	50	56	7 0 12	0	−37
2 0 1	234	263	4 0 15	188	138	7 0 13	89	−93
2 0 2	139	−134	4 0 16	0	9	7 0 14	0	33
2 0 3	338	−418	4 0 17	0	15	7 0 15	84	66
2 0 4	270	362	*4 0 18	50	−54	7 0 16	0	−1
2 0 5	415	−420	4 0 19	121	−99	7 0 17	0	9
2 0 6	220	−250	4 0 20	95	71	7 0 18	0	−28
2 0 7	504	522	4 0 21	106	82	8 0 1	115	111
2 0 8	342	345	4 0 22	0	−44	8 0 2	31	41
2 0 9	0	−14	4 0 23	0	−16	8 0 3	62	−46
2 0 10	180	−170	4 0 24	0	2	8 0 4	0	11
2 0 11	105	−95	5 0 1	192	224	8 0 5	84	−74
2 0 12	106	−82	5 0 2	0	43	8 0 6	92	−65
2 0 13	151	182	5 0 3	112	−120	8 0 7	112	94
*2 0 14	50	51	5 0 4	83	75	*8 0 8	50	52
2 0 15	197	−201	5 0 5	169	−195	8 0 9	0	−29
2 0 16	0	37	5 0 6	157	−164	8 0 10	0	7
2 0 17	0	−8	5 0 7	222	232	9 0 1	0	0
2 0 18	80	−81	5 0 8	151	152	*9 0 2	50	−67
2 0 19	149	135	*5 0 9	50	57	9 0 3	0	0
2 0 20	93	99	5 0 10	0	−17	9 0 4	0	−18
2 0 21	104	−99	5 0 11	75	−63	9 0 5	0	0
*2 0 22	50	−66	5 0 12	42	−53	10 0 1	0	−49
2 0 23	0	14	5 0 13	153	160	10 0 2	0	20
2 0 24	0	9	5 0 14	27	52	10 0 3	0	1
3 0 1	0	47	5 0 15	123	−115	11 0 1	0	35
3 0 2	254	−274	5 0 16	0	−23	11 0 2	0	5

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