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The crystal structure of WCl_6.*

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A WCl_6 compound, isostructural with UCl_6, has been identified by comparing calculated intensities with Debye-Scherrer patterns.

During the examination of a commercial‡ preparation of supposed WCl_5, the material was submitted for X-ray analysis to verify the compound designation. Chemical analyses were inconclusive in determining the W:Cl ratio because of difficulties with the reactivity of the compound. With the Debye–Scherrer techniques used, the pattern proved unidentifiable with any other tungsten-chlorine compound previously described (Reick, 1967). Other physical property measurements such as color and boiling point implied that the compound should be WCl_6. The Debye–Scherrer pattern, however, did not conform to that of WCl_6 described by Ketelaar & Oosterhout (1943).

Needle-shaped single crystals of the unknown were examined on a Buerger precession camera. The diffraction symbol proved to be $\bar{3}m\ P{-}{-}{-}$ with cell constants $a_0 = 10{\cdot}511 \pm 0{\cdot}003$, $c_0 = 5{\cdot}757 \pm 0{\cdot}001$ Å (refined values from Debye–Scherrer pattern). The only systematic reflection condition was $hk.0$ present only with $h-k=3n$. This condition must be structural because it does not conform to any conditions established by any of the allowable space groups.

Structures of similar 1:6 compounds were examined with the aid of Donnay, Donnay, Cox, Kennard & King (1963) and Wyckoff (1967). The similarity of the unit cell to that of UCl_6 reported by Zachariasen (1948) suggested a similar structure type. To test this hypothesis, powder pattern intensities were calculated using the POWD2 program of Smith (1967), with Zachariasen's UCl_6 atomic position coordinates. This calculated pattern agrees very well with the measured pattern as shown in Table 1. This agreement suggests that the unknown is isostructural with UCl_6 (space group $P\bar{3}m1$) and is thus a new polymorph of WCl_6. It can be noted that the calculated intensities also satisfy the $hk.0$ condition described.

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‡ Obtained by Gallard-Schlesinger Chemical Manufacturers, Long Island, N. Y.

Table 1. *Measured and calculated d-spacings and intensities for* WCl_6.

Observed intensities are estimated visually from the Debye–Scherrer pattern. The calculated intensities include an absorption correction for $\mu = 498\ cm^{-1}$ and a 0·3-mm-dia. spindle. In space group $P\bar{3}m1$, $hk.l$ and $kh.l$ are nonequivalent; however, no distinction between these reflections has been made in the assignment of indices.

d(calc)	d(obs)	hkℓ	I(obs)	I(calc)
5.757	5.635	00.1	< 1	0
5.255	5.166	11.0	10	10
4.865	4.818	10.1	7	6
3.881	3.832	11.1	1	1
3.570	3.458	20.1	5	4
3.034	3.007	30.0	< 1	0
2.953	2.940	21.1	4	5
2.684	2.743	30.1	6	5
2.627	2.611	22.0	2	1
2.525 2.525	2.512	31.0 11.2	4	3
2.433	2.408	20.2	<< 1	0
2.390	2.380	22.1	<< 1	0
2.312	2.307	31.1	4	3
2.208	2.197	21.2	<< 1	0
2.116	2.109	40.1	1	1
2.088 2.088	2.081	32.0 30.2	7	7
1.986	1.980	41.0	3	2
1.963	1.958	32.1	3	3
1.941	1.934	22.2	3	4
1.898	1.889	31.2	< 1	0
1.878 1.878	1.870	10.3 41.1	1	2
1.768	1.755	20.3	<< 1	1
1.751	1.749	33.0	4	4
1.736	1.732	50.1	< 1	1
1.676 1.676	1.670	33.1 21.3	3	2
1.648	1.644	42.1	1	2
1.634 1.634	1.631	51.0 41.2	3	5
1.622	1.618	30.3	< 1	2
1.573	1.570	51.1	1	1
1.528	1.525	31.3	< 1	1
1.467 1.467	1.465	60.1 40.3	1	2
1.458	1.456	52.0	1	2
1.448	1.448	43.1	< 1	1
1.439	1.433	00.4	<< 1	1
1.413 1.413	1.410	52.1 32.3	< 1	2
1.388	1.384	11.4	< 1	2
1.349	1.348	61.1	<< 1	1
1.342	1.340	60.2	1	2
1.314	1.312	44.0	< 1	1
1.300	1.300	52.2	1	1
1.281 1.281	1.280	44.1 42.3	<< 1	1
1.268 1.268	1.268	70.1 53.1	< 1	1
1.262	1.259	22.4	<< 1	1
1.244	1.243	51.3	<< 1	1
1.233	1.231	62.1	< 1	1
1.180 1.180	1.180	71.1 43.3	<< 1	1
1.165	1.164	41.4	< 1	1
1.142 1.142	1.140	54.1 10.5	<< 1	1
1.125 1.125 1.125	1.125	63.1 61.3 11.5	1	1
1.112 1.112	1.112	71.2 33.4	2	5
1.092 1.092	1.092	72.1 21.5	<< 1	1
1.077 1.077 1.077	1.076	53.3 70.3 30.5	<< 1	1
1.065	1.066	63.2	1	2
1.055 1.055	1.054	62.3 22.5	<< 1	1
1.048 1.048	1.045	81.1 31.5	<< 1	1
1.034	1.037	55.1	<< 1	0
1.024	1.023	52.4	< 1	2
1.011	1.009	90.0	<< 1	1
1.008 1.008	1.006	73.1 32.5	<< 1	1
0.9962 0.9962 0.9962	0.9937	90.1 54.3 41.5	<< 1	1
0.9873	0.9875	55.2	< 1	2
0.9787	0.9790	82.1	<< 1	1
0.9704	0.9685	44.4	<< 1	1
0.9568	0.9557	42.5	< 1	1
0.9414 0.9414 0.9414	0.9423	91.1 65.1 51.4	< 1	2
0.9389 0.9389	0.9402	82.2 20.6	< 1	2
0.9315 0.9315	0.9318	74.1 81.3	<< 1	1
0.9242	0.9229	71.4	<< 1	1
0.9126 0.9126	0.9115	83.1 43.5	< 1	2
0.9013	0.9037	22.6	< 1	1
0.8969 0.8969	0.8975	74.2 63.4	1	3
0.8862 0.8862	0.8870	92.1 61.5	<< 1	1
0.8759	0.8766	66.0	< 1	1
0.8640 0.8640	0.8646	10,1.0 41.6	1	3
0.8621 0.8621 0.8621	0.8627	75.1 70.5 53.5	1	3
0.8544 0.8544	0.8544	65.3 91.3	< 1	1
0.8327 0.8327 0.8327	0.8324	93.1 83.3 71.5	< 1	1
0.8275	0.8277	90.4	< 1	2
0.8175	0.8168	82.4	< 1	2
0.8093	0.8098	10,2.1	< 1	2
0.8077	0.8078	93.2	1	3
0.8015 0.8014	0.8020	85.0 52.6	< 1	2
0.7999 0.7999 0.7999	0.8002	75.1 72.5 21.7	< 1	2
0.7820 0.7820 0.7820 0.7820	0.7808	11,1.1 94.1 81.5 31.7	< 1	2