into the α-$Cu(NO_3)_2$ structure can be seen in the structures of $Cu(NO_3)_2.CH_3NO_2$ (Duffin & Wallwork, 1966) and the present work respectively. Anhydrous α-cupric nitrate contains copper atoms in a distorted octahedral (4+1+1) arrangement with all the nitrato groups acting as bridging ligands between adjacent copper atoms and each forming two strong Cu–O bonds. Half the nitrato groups, however, form two additional, weaker, bonds to copper in order to complete the copper coordination sphere. The introduction of the nitromethane molecule into the copper sphere, in the fifth octahedral position, allows all the nitrato groups to act solely as bridging groups between adjacent copper atoms while the copper coordination remains essentially a (4+1) tetragonal pyramidal arrangement. Thus the nitromethane molecules relieve some of the steric hindrance involved in the α-$Cu(NO_3)_2$ structure without affecting the strength of the main Cu–O bonds. The tetragonal pyramidal coordination of the copper atom is maintained in the $Cu(NO_3)_2.2CH_3CN$ structure although the strong methyl cyanide ligands have replaced two nitrato oxygen atoms in the copper square plane. This has resulted in a weakening of the copper–nitrate bonding so that although half the nitrato groups act as bridging ligands between adjacent copper atoms they form only one strong and one weaker Cu–O bond, the weaker bonds being directed towards the apex of the copper tetragonal pyramids. The remaining nitrato groups are essentially unidentate ligands and form only one strong bond to copper. Presumably steric hindrance prevents these groups from acting as bidentate ligands and completing an octahedral copper coordination.

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The Structures of Uranyl Chloride and its Hydrates

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X-ray powder diffraction data for UO_2Cl_2, $UO_2Cl_2.H_2O$ and $UO_2Cl_2.3H_2O$ are presented, together with the unit cells derived from these data. The structures of the three compounds are also given, with some restrictions about the positions of the oxygen ions. From the structure determination it follows that $UO_2Cl_2.H_2O$ is not a true hydrate.

As part of a study of uranyl chloride (UO_2Cl_2) and its two hydrates ($UO_2Cl_2.H_2O$ and $UO_2Cl_2.3H_2O$) the X-ray powder diffraction patterns of these compounds were indexed and an attempt was made to determine their structures. The diffraction patterns were recorded with a Guinier–de Wolff focusing camera using Cu $K\alpha$ radiation. The intensities were measured on a densitometer as peak values and integrated values were ob-

Table 1. *Space groups and unit cells* (*standard deviations in parentheses*)*

Compound	Symmetry and space group	*a*	*b*	*c*	*β*	*Z*
UO_2Cl_2	Orthorhombic; *Pnma*	5·725 (1)	8·409 (2)	8·720 (2)		4
$UO_2Cl_2.H_2O$	Monoclinic; $P2_1/m$	5·836 (3)	8·563 (3)	5·566 (2)	97·70° (3)	2
$UO_2Cl_2.3H_2O$	Orthorhombic; *Pnma*	12·738 (5)	10·495 (5)	5·547 (2)		4

* The unit cell of UO_2Cl_2 has been found previously by Baenziger & Rundle (1944). The present data are in good agreement with their result; this implies that the data in the ASTM Powder Data File, given by Dunn (1956) are in error.

Table 2. *Q values and intensities expressed as* $j \times \mathrm{Lp} \times F^2 \times 10^{-4}$ *(F in electrons per unit cell) for* UO_2Cl_2

Unobserved reflexions are marked with an asterisk.

hkl	Q_{obs}	Q_{calc}	I_{obs}	I_{calc}	$\sum_r I_{\mathrm{calc}}$
011	273	274	1023	861	
101	438	437	2864	2817	
002	526	527	619	607	
020	566	567	959	862	
111	579	579	717	666	
102	830	832	468	467	
112	973	974	908	949	
121	1003	1004	1163	1193	
022	1093	1093	492	494	
200	1222	1222	36	62	
013	1325	1327	396	479	
201	1354	1353	110	123	
210	1365	1364	200	211	
122	1402	1398	405	2	315
031		1406		313	
103	1493	1491	136	15	127
211		1495		112	
131	1711	1711	419	396	
202	1749	1748	72	77	
220	1786	1788	237	270	
212	1890	1890	256	296	
221*	-	1920	3	3	
123	2057	2057	80	109	
132	2110	2106	495	516	527
004		2107		11	
040	2262	2265	347	308	
222	2315	2314	91	105	
203	2406	2406	276	293	361
104		2412		68	
033	2459	2459	356	340	
230	2497	2495	190	213	
213	2553	2548	612	263	705
114		2553		442	
231*	-	2627	14	16	
024*	-	2672	14	36	
141	2704	2702	449	427	
133*	-	2764	8	8	
042	2793	2791	155	128	
301*	-	2880	2	2	
223	2976	2972	262	163	256
124		2977		93	
311	3024	3021	391	289	430
232		3022		141	
142	3094	3096	53	62	
302	3274	3275	58	81	
204*	-	3327	1	1	
312*	-	3416	15	27	
015	3432	3432	153	174	
321	3444	3446	32	87	
214*	-	3469	0	0	
240	3482	3486	53	48	
105*	-	3596	16	34	
241*	-	3617	16	30	
015		3670		10	
233	3682	3680	367	95	350
134		3685		245	
115*	-	3737	3	3	
143*	-	3754	16	17	
322	3841	3840	159	139	
224*	-	3893	16	16	
303	3934	3932	25	23	
151	3972	3975	30	17	
242	4010	4012	56	45	
313*	-	4074	17	26	
331	4151	4153	187	164	182
125		4162		18	
152	4370	4369	131	69	70
044		4370		1	
323*	-	4498	0	0	
205	4513	4511	46	27	
332*	-	4548	1	1	
035	4560	4564	59	64	
234*	-	4600	16	16	
215		4653		72	
243	4661	4670	315	143	257
144		4675		42	
053	4728	4722	84	47	71
006		4738		24	
250	4761	4759	30	17	
304	4855	4853	149	97	114
135		4869		17	
400*	-	4885	3	3	
251*	-	4890	17	26	
314		4996		23	
401	5016	5016	232	4	177
410		5026		116	
153		5027		34	

Table 3. *Q values and intensities for* $UO_2Cl_2.H_2O$, *expressed as in Table* 2

Unobserved reflexions are marked with an asterisk.

hkl	Q_{obs}	Q_{calc}	I_{obs}	I_{calc}	$\sum_r I_{\mathrm{calc}}$
100	299	299	602	576	
001	329	329	655	615	
110	436	436	301	267	
011	465	466	190	160	
$10\bar{1}$	545	544	738	503	767
020		546		264	
$11\bar{1}$*	-	681	1	1	
101	711	712	22	22	
120	848	845	442	226	457
111		849		231	
021	877	875	174	165	
$12\bar{1}$	1090	1090	100	102	
200*	-	1197	1	1	
121	1257	1258	120	128	
002	1328	1315	101	10	115
210		1333		105	
$20\bar{1}$	1356	1357	33	40	
$10\bar{2}$	1447	1446	104	62	128
012		1452		66	
$21\bar{1}$	1494	1494	31	36	
130	1527	1527	125	113	
031	1558	1557	81	77	
$11\bar{2}$	1584	1583	11	17	
201	1697	1694	9	4	
220	1738	1742	43	33	
$13\bar{1}$*	-	1772	0	0	
102*	-	1783	2	2	
211	1828	1830	132	127	
022	1863	1861	48	43	
$22\bar{1}$	1904	1903	74	55	
112	1923	1919	133	131	
131	1945	1940	89	111	
$12\bar{2}$	1992	1992	27	18	
$20\bar{2}$	2182	2176	137	58	147
040		2183		89	
221	2234	2239	8	7	
$21\bar{2}$*	-	2312	0	0	
122	2325	2328	10	13	
230	2425	2424	63	59	
140	2484	2482	61	61	
041	2517	2512	66	66	
032	2543	2543	49	54	
$23\bar{1}$	2584	2585	40	37	
$13\bar{2}$	2679	2674	18	17	
300*	-	2692	4	4	
$22\bar{2}$	2724	2721	99	26	103
$14\bar{1}$		2727		77	
$30\bar{1}$*	-	2769	0	0	
310	2822	2829	46	36	
202*	-	2848	5	8	
141		2895		10	
$31\bar{1}$	2912	2905	101	42	95
231		2921		43	
003*	-	2959	3	3	
212	2987	2984	50	61	
$10\bar{3}$	3014	3006	51	7	60
132		3010		53	
013	3108	3096	51	44	
$11\bar{3}$	3140	3143	20	21	
320*	-	3238	0	0	
301	3275	3273	5	5	
$32\bar{1}$	3311	3315	13	11	
240		3379		1	
222	3393	3394	53	11	40
$23\bar{2}$		3403		1	
311		3409		27	
042		3498		6	
$30\bar{2}$	3501	3503	25	11	27
023		3505		2	
103		3511		8	
$24\bar{1}$	3546	3540	31	18	32
$12\bar{3}$		3552		14	
$31\bar{2}$		3639		15	
113	3646	3647	75	27	68
$20\bar{3}$		3652		26	
321	3814	3819	45	14	
303		4895		14	
060	4913	4911	82	12	57
$41\bar{1}$		4915		20	
410		4922		11	
152		5193		21	
223	5214	5205	56	19	52
160		5210		12	
$10\bar{4}$		5224		0	

Table 4. *Q values and intensities for* $UO_2Cl_2.3H_2O$, *expressed as in Table* 2

Unobserved reflexions are marked with an asterisk.

hkl	Q_{obs}	Q_{calc}	I_{obs}	I_{calc}	$\sum_r I_{\mathrm{calc}}$
200	246	246	130	1	
210	337	337	3933	3976	
020	364	363	1756	1533	
101	387	386	1172	1154	
011	416	415	2350	2273	
111	477	477	1556	1523	
201	571	571	1163	1135	
220	610	609	86	177	
211	662	662	159	47	
121	750	749	567	427	
301	880	879	373	426	
221	934	934	1079	1116	
311	969	970	719	732	
400	987	985	362	345	
230	1062	1063	1052	1054	
410	1076	1076	106	20	
031	1141	1141	201	290	
131	1203	1203	309	264	
321*	-	1242	20	42	
002	1310	1299	84	33	51
401		1310		18	
420	1349	1349	525	471	
102	1360	1361	303	324	
231*	-	1388	11	11	
411	1402	1401	601	619	
112	1452	1451	747	327	937
040		1452		610	
202	1545	1545	87	71	
212	1634	1636	60	1	
022	1666	1662	40	25	
421*	-	1673	16	16	
331	1696	1696	313	269	318
240		1698		49	
122	1724	1724	181	166	
430	1805	1802	76	91	
302	1854	1854	251	305	
501	1865	1865	121	85	
222*	-	1909	16	16	
312	1946	1944	350	340	360
511		1956		20	
241	2023	2023	532	547	
431	2125	2127	466	451	
132	2177	2178	413	331	
322	2217	2217	456	429	431
600		2218		2	
521	2229	2228	513	555	
402*	-	2285	0	0	
610	2307	2309	299	299	
341	2331	2331	121	107	
232	2360	2362	50	14	
412*	-	2376	5	5	
250	2514	2515	313	348	
601	2544	2543	170	158	
620	2581	2581	82	54	
051	2592	2593	159	98	
611*	-	2634	16	16	
422	2653	2648	132	12	163
151		2655		151	
332	2670	2671	142	100	
531*	-	2682	21	23	
042*	-	2751	21	39	
441*	-	2763	7	7	
142	2811	2813	148	162	
502	2839	2840	70	38	41
251		2840		3	
621	2904	2906	118	202	
512	2929	2930	307	356	
103	2982	2985	50	20	
242*	-	2998	8	8	
013	3015	3014	65	62	
630	3035	3035	112	125	
113	3073	3076	129	62	
432*	-	3102	2	2	
351	3149	3148	108	77	
203	3171	3170	114	105	
522	3205	3203	89	58	
450		3255		9	
213	3270	3261	126	0	78
060		3267		69	
342	3314	3306	207	140	189
541		3317		49	
701		3344		13	
123	3349	3348	200	139	169
631		3360		17	
711	3438	3435	127	76	
303*	-	3478	15	15	
260		3514		8	
602	3532	3517	145	10	92
223		3533		74	
313	3570	3569	201	147	
451	3582	3579	189	167	
612*	-	3608	2	2	
152	3631	3630	174	139	
161		3653		41	
532	3659	3657	282	208	249
640		3670		0	
721*	-	3707	22	33	
442	3739	3737	60	4	40
033		3740		36	
133	3799	3802	110	46	46
252		3814		0	
261	3841	3838	209	110	241
323		3841		104	
622*	-	3881	7	7	
403*	-	3909	3	3	
233	3996	3987	137	0	59
641		3995		59	

tained by use of an empirical graph of the width *versus* 2θ. These values were corrected for absorption and the Guinier geometry after Mirkin (1964) and Sas & De Wolff (1966). The unit cells of the three compounds and their space groups are listed in Table 1, and measured and calculated values of $Q = 10^4/d^2$ in Tables 2, 3 and 4. Tables 2, 3 and 4 also contain the observed intensities (corrected as mentioned above) and the calculated intensities resulting from the least-squares refinements.

The structure determinations were based on three-dimensional Patterson syntheses, from which the uranium positions were found and which indicated the chlorine positions for the anhydrous compound and the monohydrate. Geometrical considerations then led to a plausible model also for the oxygen atoms. For the trihydrate the positions of the lighter atoms could not be deduced from the Patterson synthesis. From geometrical considerations several models could be derived of which all but one were ruled out by subsequent refinement.

The three models were refined by a full-matrix least-squares method, minimizing the quantity $\sum_i (\sum_r I_{\mathrm{obs}} - \sum_r I_{\mathrm{calc}})^2$, where $\sum_i$ is the sum over all measured lines, single or composite, and $\sum_r$ the sum over all single reflexions in a composite line. The intensities of unobserved reflexions were made equal to one half of that of the weakest observed reflexion; if the calculated intensity was smaller than this the program made the 'observed' value equal to the calculated one.

The scattering factors were taken from Cromer & Waber (1964), supplemented by the coefficients for anomalous dispersion. Overall isotropic temperature factors were used in the refinements. In view of the method used to obtain the intensities the final values of the temperature factors have no physical significance. The refinements resulted in R values of 10·0%, 8·9% and 11·1% for the anhydrous compound, the monohydrate and the trihydrate, respectively, R being defined as $\sum_i (I_{\text{obs}}-I_{\text{calc}})/\sum_i I_{\text{obs}}$.

The final coordinates of the atoms and the temperature factors are listed in Tables 5, 6 and 7, together with their standard deviations (in parentheses).

Table 5. *Fractional atomic coordinates and overall isotropic temperature factor in* UO_2Cl_2; *standard deviations in parentheses*

	Position	*x/a*	*y/b*	*z/c*
U	4(*c*)	0·067 (2)	0·25	0·064 (1)
Cl	8(*d*)	0·170 (5)	0·955 (3)	0·124 (3)
O(1)	4(*c*)	0·870 (22)	0·25	0·208 (11)
O(2)	4(*c*)	0·279 (19)	0·25	0·997 (10)
B			0·8 (3)	

Table 6. *Fractional atomic coordinates and overall isotropic temperature factor in* $UO_2Cl_2.1H_2O$; *standard deviations in parentheses*

	Position	*x/a*	*y/b*	*z/c*
U	2(*e*)	0·091 (2)	0·25	0·080 (3)
Cl	4(*f*)	0·211 (6)	0·536 (4)	0·164 (7)
O(1)	2(*e*)	0·237 (21)	0·25	0·869 (24)
O(2)	2(*e*)	0·895 (25)	0·25	0·192 (21)
O(3)	2(*e*)	0·273 (16)	0·25	0·401 (20)
B			2·0 (5)	

Table 7. *Fractional atomic coordinates and overall isotropic temperature factor in* $UO_2Cl_2.3H_2O$; *standard deviations in parentheses*

	Position	*x/a*	*y/b*	*z/c*
U	4(*c*)	0·116 (1)	0·25	0·130 (2)
Cl	8(*d*)	0·182 (3)	0·012 (3)	0·033 (6)
O(1)	4(*c*)	0·177 (9)	0·25	0·393 (27)
O(2)	4(*c*)	0·032 (9)	0·25	0·910 (27)
O(3)	4(*c*)	0·294 (9)	0·25	0·977 (18)
O(4)	8(*d*)	0·963 (5)	0·125 (7)	0·329 (15)
B			2·5 (5)	

In all three compounds the uranium ion and two oxygen atoms form a uranyl ion. Five other neighbours surround the uranium approximately in a plane perpendicular to the uranyl bonds. In the anhydrous compound and the monohydrate four of these are chlorine, in the trihydrate two. The U–Cl distances are in good agreement with the sum of the ionic radii (2·64 Å). In the trihydrate the three U–O distances in the above mentioned plane are 2·4–2·6 Å, corresponding to relatively weak bonds. In the monohydrate, however, the distance between uranium and the 'water molecule' is so small (1·95 ± 0·10 Å) that this compound cannot be a true hydrate.

All calculations were performed on an Electrologica X8 computer. The programs for the Patterson syntheses, the least-squares refinements, the calculations of the cell constants and the distances and angles were written by Dr H. M. Rietveld of this institute.

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