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The Crystal Structure of $ReCl_5$

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$ReCl_5$ forms monoclinic crystals with lattice constants: $a=9{\cdot}24$, $b=11{\cdot}54$, $c=12{\cdot}03$ Å; $\beta=109{\cdot}1°$. The space group is $P2_1/c$, and the unit cell contains eight $ReCl_5$ units. Full-matrix, least-squares refinement of diffractometrically measured X-ray diffraction data resulted in a final R of 9·3% (all reflections). The structure is based on a double-hexagonal closest packing of chlorine atoms, in which rhenium atoms occupy one-fifth of the octahedral holes. Two such octahedra share an edge to form a dimeric Re_2Cl_{10} unit. The Re–Cl bond distances involving bridging Cl average to $2{\cdot}465\pm0{\cdot}013$ Å; the average bond length to nonbridging Cl is $2{\cdot}244\pm0{\cdot}012$ Å. Rhenium atoms in the Re_2Cl_{10} units are each shifted by about 0·20 Å from the centers of the octahedra in directions away from one another. The packing mode of Cl in $ReCl_5$ contrasts with a hexagonal closest packing of Cl in $TaCl_5$ and a cubic closest packing of Cl in UCl_5. Of these, $ReCl_5$ exhibits both the highest density and the smallest interatomic distances.

Introduction

Four compounds in the rhenium–chlorine system are known (Colton, 1965): $ReCl_3$, $ReCl_4$, $ReCl_5$ and $ReCl_6$. The pentachloride is a dark brown to black material, melting at 220°C. It is moisture-sensitive and highly reactive; a few of its chemical reactions have recently been investigated (Cotton, Robinson & Walton, 1967).

Our interest in $ReCl_5$ stems from the variety of crystal structures assumed by the pentachlorides. Examples include: ionic structures – PCl_4^+ and PCl_6^- in PCl_5 (Powell, Clark & Wells, 1940); trigonal, bipyramidal molecules – $SbCl_5$ (Ohlberg, 1959); bridged M_2Cl_{10} dimers – $NbCl_5$ (Zalkin & Sands, 1958); $MoCl_5$ (Sands & Zalkin, 1959); UCl_5 (Smith, Johnson & Elson, 1967); and infinite chains of edge-shared pentagonal bipyramids – $PaCl_5$ (Dodge, Smith, Johnson & Elson, 1967). Five-coordination, we note, is avoided in all except $SbCl_5$. The present investigation shows $ReCl_5$ to be of the bridged-dimer type, but of a different crystallographic variety.

Experimental

Our sample of $ReCl_5$ was kindly provided by Dr D. Brown of the Atomic Energy Research Establishment, Harwell, England. Dr Brown informed us that the material was prepared by the thermal decomposition of $ReCl_6$ in a dry nitrogen atmosphere. Microscopic examination of the sample-tube showed a number of suitably sized crystals. The tube was opened in a dry-box and a half-dozen or so crystals were sealed off in thin-walled glass capillaries for X-ray examination. The reactive nature of $ReCl_5$ was evidenced by the fact that samples left open overnight in the dry-box developed traces of a brown liquid (possibly $ReOCl_4$).

Single-crystal diffraction photographs showed monoclinic symmetry; the systematic extinctions ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$) are those uniquely characterizing the space group $P2_1/c$ (*International Tables for X-ray Crystallography*, 1952). Refined values of the lattice constants are (Mo $K\alpha=0{\cdot}7107$ Å); $a=9{\cdot}24$, $b=11{\cdot}54$, $c=12{\cdot}03$ Å; $\beta=109{\cdot}1°$ (probable errors estimated as about 0·3%). The density calculated for eight $ReCl_5$ units per unit cell is 3·98 g.cm^{-3}.

Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a goniostat. The crystal specimen was an irregularly shaped plate, approximately 0·22 mm in length and $0{\cdot}14\times0{\cdot}07$ mm in cross section. The stationary crystal–stationary counter technique (Furnas, 1957) was used; the radiation was Zr-filtered Mo $K\alpha$. A total of 1127 reflections were recorded up to a 2θ-cutoff of 40°. Because of the irregular shape of the crystal and a rather large linear absorption coefficient ($\mu=233$ cm^{-1} for

Mo $K\alpha$), reflections at $\chi=90°$ showed a pronounced variation of intensity with φ. For example, the overall variations of the 020 and 040 reflections were 4:1 and 6:1, respectively, lowest readings being obtained when the thickest parts of the crystal were presented to the X-ray beam. The intensity variation with φ of these two reflections provided corrective factors which were applied to all reflections. These corrections, admittedly approximate, nevertheless proved to be remarkably effective (see below). Finally, the intensities were converted to relative $|F|$'s through the application of Lorentz–polarization factors.

Determination of structure

The most reasonable calculated density (3·98 g.cm^{-3}) was for eight units of $ReCl_5$ per unit cell. A partial corroboration came from volume considerations. In closest-packing, each Cl atom requires about 34 Å^3. Division of this number into the cell volume indicated about 36 Cl atoms within the unit cell. The first nine largest peaks in the three-dimensional Patterson function were very satisfactorily accounted for by vector interactions between two fourfold Re atoms: Re(1) at 0·31, 1/8, 0·29 and Re(2) at −0·11, 1/8, 0·19. A structure-factor calculation based on these two atoms gave an R-value of 29%; ten fourfold Cl atoms were readily located in a 'heavy-atom' electron-density synthesis. Individual isotropic temperature factors being employed, there are 49 parameters to be determined from the 1127 measured reflections.

The structure model was refined by the full-matrix, least-squares program of Gantzel, Sparks & Trueblood (ACA Program no. 317, unpublished). The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962) for neutral Re and singly-ionized Cl. The quantity minimized was $\Sigma w(|F_o|-1/K|F_c|)^2$ where K is the scale factor relating $|F_o|$ and $|F_c|$ and the w's are given by the following weighting scheme (Smith, Johnson & Nordine, 1965): $w=F_o^{1/4}, F_o<A$; $w=A^{5/4}F_o^{-1}, F_o>A$. When the structure factors were placed on an absolute scale, $A=186$. Five cycles of refinement reduced the R index $(=\Sigma(K|F_o|-|F_c|)/\Sigma K|F_o|)$ to 9·3% (all reflections). Changes in parameter values in the last cycle were $\leq 0{\cdot}001$ times the standard deviations.

There is some indication of extinction effects in the stronger reflections, and for the weaker reflections it appears that the background may have been generally slightly underestimated. In view of the approximate nature of the absorption corrections, these effects were not investigated further. Nevertheless the largest peak in a final difference synthesis amounted to only 1·0 e.Å^{-3}. To test the effectiveness of the absorption corrections, a refinement series was carried out on the un-

Table 1. *Final parameters in* $ReCl_5$

All atoms in general positions; e.s.d.'s in parentheses.

	10^4x	10^4y	10^4z	B
Re(1)	3087 (2)	1233 (2)	2928 (1)	2·1 ± 0·1 Å^2
Re(2)	−1192 (2)	1287 (2)	1853 (1)	2·0 ± 0·1
Cl (1)	910 (12)	138 (9)	1596 (9)	2·1 ± 0·2
Cl(2)	2832 (13)	146 (11)	4400 (10)	2·8 ± 0·2
Cl(3)	2911 (13)	−4912 (11)	4367 (10)	2·6 ± 0·2
Cl(4)	5254 (15)	−4974 (13)	2445 (12)	3·9 ± 0·3
Cl(5)	981 (13)	−4818 (11)	1567 (10)	3·0 ± 0·2
Cl(6)	945 (12)	2405 (10)	3158 (9)	2·5 ± 0·2
Cl(7)	4848 (15)	2416 (13)	4174 (12)	4·0 ± 0·3
Cl(8)	2897 (13)	−2547 (11)	2780 (10)	2·9 ± 0·2
Cl(9)	976 (14)	−2635 (12)	4631 (11)	3·4 ± 0·3
Cl(10)	2919 (14)	2374 (11)	1372 (11)	3·4 ± 0·3

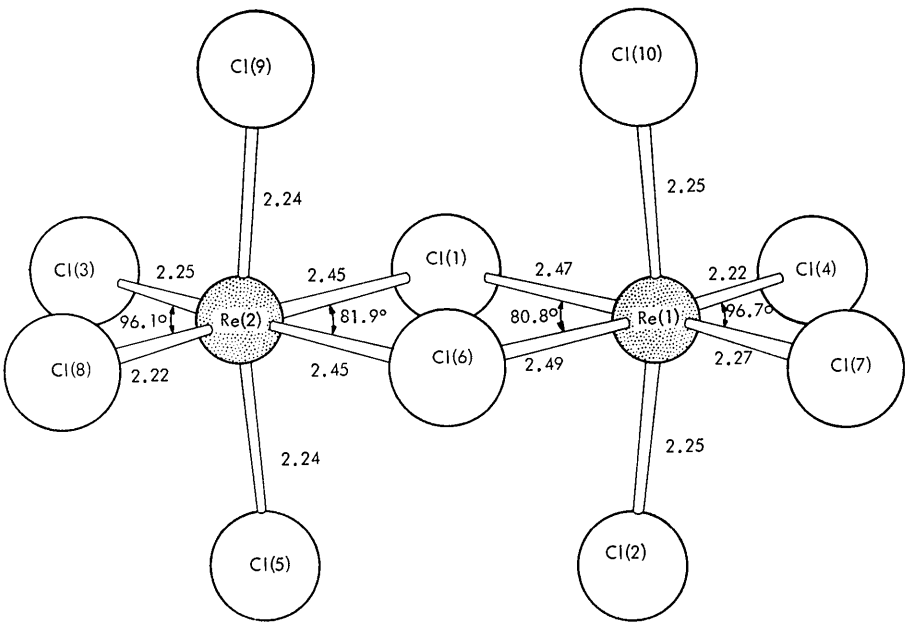

Fig. 1. Configuration of Re_2Cl_{10} dimer. Distances in Å.

corrected $|F_o|$'s. The R value for this refinement was 22·6%, and the ΔF's exhibited a decided φ-dependency.

Parameters from the $R = 9{\cdot}3\%$ refinement were accepted as final, and are given in Table 1.* Table 2 lists observed and calculated structure factors.

Discussion of structure

Each rhenium atom is coordinated octahedrally to six chlorine atoms; two such octahedra share an edge to form the Re_2Cl_{10} unit illustrated in Fig. 1. The symmetry thereof does not differ sensibly from *mmm*, although no crystallographic symmetry is required. This dimeric configuration is very similar to those found in the solid state for $NbCl_5$ and $TaCl_5$ (Zalkin & Sands, 1958), $MoCl_5$ (Sands & Zalkin, 1959) and UCl_5 (Smith, Johnson & Elson, 1967). $ReCl_5$, however, is not isomorphous with any of the aforementioned compounds.

The eight independent Re–Cl bond lengths involving nonbridging Cl average to $2{\cdot}244 \pm 0{\cdot}012$ Å. Individual values are listed in Table 3. Re–Cl bond lengths to the bridging chlorine atoms, Cl(1) and Cl(6), are significantly longer at $2{\cdot}465 \pm 0{\cdot}013$ Å (average of four). Similar variations between bonds to bridging and nonbridging Cl are also found in the pentachlorides of Nb, Mo, Ta and U. We note that both independent Re atoms display rather similar bond distances. While this does not necessarily mean that both are in the same oxidation state, there is, at least, little evidence to consider the rhenium atoms as, say, Re^{IV} and Re^{VI}.

There is little in the literature with which the present bond lengths can be compared. $MRe^{V}Cl_6$ compounds might provide suitable distances (if, in fact, $ReCl_6$ octahedra are present); however, no structural data seem to be available. For the irregular octahedral molecules, $ReOCl_3[P(C_2H_5)_2C_6H_5]_2$ (Ehrlich & Owston, 1963) and $ReNCl_2[P(C_2H_5)_2C_6H_5]_2$ (Corfield, Doedens & Ibers, 1967), the Re^{V}–Cl bond lengths are 2·41–2·47 Å in the former and $2{\cdot}454 \pm 0{\cdot}004$ and $2{\cdot}563 \pm 0{\cdot}004$ Å in the latter. However, Corfield *et al.* (1967) point out that there is evidence of multiple bonding between Re and N (or O) in these molecules, and hence, the Re–Cl (and Re–P) bond lengths are longer than

* Anomalous dispersion effects proved of no importance in the present case. A refinement series employing real and imaginary terms in the scattering factor for Re (values from Cromer (1965)) gave an R index of 9·2%. Variable parameters were, in the worst cases (namely for the B's), within $\frac{1}{2}\sigma$ of their values without dispersion. Bond data, thus, are unaffected at the present level of accuracy.

Table 2. *Calculated and observed structure factors*

H,K= 0, 0	H,K= 0, 7	-8 25 20	8 5 11	4 16 16	6 23 -2	6 25 14	-9 108-106	-9 122 116	H,K= 4, 1		-6 49 -50	6 169 160	-4 32 27	-3 150-179	-5 38 50
L FOR FCA	L FOR FCA	-7 98 -93	9 15 -16		7 65 -56	7 52 47	-8 30 26	L FOR FCA	H,K= 4, 5	-4 244-242	-3 118 133	-2 8 14	-4 26 5
2 438-441	1 53 -26	-6 65 56	H,K= 1,11		8 57 -55		-7 21 -24	-7 21 19	-11 23 12	L FOR FCA	-2 372 377	H,K= 5, 5	-2 58 -53	0 30 -7	-3 12 -16
4 77 78	2 31 15	-5 231 228	H,K= 1, 6		9 78 74	H,K= 2, 8	-6 4 -2	-6 27 -32	-10 11 6	-10 17 1	0 617-617	L FOR FCA	-1 45 -30	0 9 -16	-2 70 79
6 158 148	3 59 -60	-4 282-282	L FOR FCA	-1 53 -47		L FOR FCA	-5 160 159	-5 111-108	-9 36 -27	-9 63 -51	0 39 -15	1 123 129	-1 31 11
8 304-299	4 20 17	-3 313-310	-9 23 15	0 38 -48	H,K= 2, 4	-4 26 -20	-4 4 10	-8 37 34	-8 37 -29	4 103 98	-8 21 28	1 55 -23	2 38 -14	0 118-115
10 119 111	5 14 10	-2 3 2	-8 17 -17		L FOR FCA	-7 50 -35	-7 171 173	-3 165 167	-7 103 98	-7 9 -2	6 140-139	2 80 62		1 38 24
	6 47 -44	-1 254 257	-7 59 -60	H,K= 2, 0	-10 71 -65	-6 12 12	-2 349 357	-2 202 201	-6 149-145	-6 16 12		3 44 31	H,K= 6, 7	2 153 141
H,K= 0, 1	8 47 40	0 6 -9	-6 97 -99	L FOR FCA	-9 45 46	-5 24 -20	-1 114 107	-1 86 -96	-5 129-130	-5 32 29	H,K= 5, 1	-5 30 8	4 47 -28	L FOR FCA
L FOR FCA	8 106 92	1 61 47	-5 215-210	-10 54 51	-8 64 60	-4 13 8	0 53 12	0 24 -25	-4 114-118	-4 23 -16	L FOR FCA	-4 16 12	5 37 -8	-6 98 95	H,K= 7, 5
1 29 25		2 19 18	-4 155-147	-8 50 -37	-7 34 -14	-2 39 -37	1 42 -28	1 15 5	-3 62 57	-3 33 -35	-11 112-105	-3 17 -8		-5 149-153	L FOR FCA
2 60 -59	H,K= 0, 8	3 291-289	-3 282 280	-6 12 13	-6 13 -5	-2 36 30	2 69 -67	2 34 5	-2 34 19	-2 35 33	-10 30 19	-2 25 -9	H,K= 6, 2	-4 25 -27	-7 134-134
3 32 -31	L FOR FCA	-2 25 -27	-4 21 7	-5 64 -67	-1 9 -13	3 27 5	3 32 -10	-1 57 42	-1 71 -82	-9 90 94	-1 32 -7	L FOR FCA	-3 95 108	-6 85 88
4 25 27	0 520 519	5 397 400	-1 135-123	-2 66 58	-4 16 -12	0 84-108	4 32 -20	4 50 -45	0 129-116	-8 62 -62	0 41 -55	-10 27 -25	-4 59 55	-5 35 34
5 27 -22	1 35 -24	6 13 5	0 8 22	0 229-189	-3 20 30	1 59 -51	5 46 -37	5 32 26	1 158-132	-7 41 -35	1 25 -12	-9 42 -39	-1 36 12	-4 33 20
6 39 36	2 277-260	7 298-303	1 38 -44	2 145 131	-2 42 -45	2 105 104	6 56 -42	6 43 -23	2 216 221	2 151-171	-6 11 -10	2 59 -48	-8 21 8	0 40 -6	-3 57 64
7 103 91	3 8 10	8 25 6	2 21 0	4 138-141	-1 51 -56	3 42 30	7 71 71	7 66 -58	3 153 165	3 189-188	5 24 11	3 37 16	-7 151 149	1 37 -36	-2 114-120
8 140-128	4 61 58	9 76 77	3 273 273	6 28 32	0 157 142	4 94 -96	8 134-132		4 76 -76	4 249 244	-4 42 40	4 26 11	-6 33 -25		-1 117-125
9 121-122	5 19 22	10 15 -16	4 25 2	8 156 153	1 61 -53	5 45 48		H,K= 3, 7	5 117-116	5 142 138	-3 24 -7	5 65 -54	-5 214-219	H,K= 6, 8	0 140 140
10 51 41	6 101 89		5 261-272	6 27 14	2 281-276	6 27 14	H,K= 3, 3	L FOR FCA	6 61 53	6 101 -95	-2 27 -9		-4 132 130	L FOR FCA	1 130 117
H,K= 0, 2	7 35 -28	H,K= 1, 3	6 25 16	H,K= 2, 1	3 63 63		L FOR FCA	-6 21 10	7 26 18		-1 61 51	H,K= -5, 6	-3 164 179	-4 108-111	
L FOR FCA		L FOR FCA	7 171 155	L FOR FCA	4 167 151	H,K= 2, 9	-11 91 75	-7 5 -6	8 30 35	H,K= 4, 6	0 56 -57	L FOR FCA	-2 35 -8	-3 6 -1	H,K= 7, 6
H,K= 0, 9	H,K= 0, 9	-10 86 -77	8 18 -2	-11 82 -78	5 11 0	L FOR FCA	-10 116 109	-6 71 68		L FOR FCA	1 78 -70	-8 21 19	-1 48 -52	-2 87 105	L FOR FCA
0 11 -8	L FOR FCA	-9 32 -27		-10 111 106	6 33 26	-5 134 128	-9 64 -65	H,K= 4, 2	-9 175-169	2 52 33	-7 52 41	0 29 -11	-1 13 -35	-4 19 -17
1 479-575	1 29 19	-8 37 -32	H,K= 1, 7	-9 172 166	7 26 5	-5 84 78	-8 33 -33	-4 148-157	L FOR FCA	-8 5 1	3 37 15	-6 5 -5	1 152-143	-5 20 17
2 12 5	2 58 -36	-7 122 123	L FOR FCA	-8 183-174	8 115-110	-4 32 -31	-7 29 -24	-3 227 226	-11 30 -21	-7 206 199	4 52 35	-5 89 90	2 46 -13	H,K= 7, 0	-4 16 9
3 236 233	3 22 9	-6 205 201	-8 37 27	-7 236-224	9 22 7	-3 92 90	-2 122 122	-2 122 122	-10 -11	5 54 41	-4 5 -10	3 234 238	L FOR FCA	-3 31 33
4 4 -6	4 33 42	-5 195-192	-7 88 -88	-6 230 220		-2 92 -87	-5 186 181	-1 166-192	-9 196 188	-5 187-206	6 74 -69	3 255-269	4 39 -5	-8 16 -3	-2 31 29
5 49 48	5 30 -33	-4 413-426	-6 98 -91	-5 169 157	H,K= 2, 5	-1 118-123	-4 254 254	0 52-108	-8 10 -15	-4 29 -30		-2 6 4	5 228-216	-6 18 3	-1 90 -96
6 30 -14	6 25 8	-3 197 190	-5 217 211	-6 60 -60	L FOR FCA	0 136 172	-3 286-290	1 49 65	-7 344-348	-3 130 136	H,K= 5, 2	-1 199 247		-4 43 39	0 9 8
7 237-233		-2 173 168	-3 58 58	-10 153-147	1 122 135	-2 415-410	2 27 -4	-6 4 -5	-2 36 43	L FOR FCA	0 21 -3	H,K= 6, 3	-2 100 -91	
8 36 -7	H,K= 0,10	-1 130-123	-3 209-204	-2 168-167	-9 194-189	2 102-103	-1 280 286	3 77 71	-5 315 318	-1 74 78	-10 60 62	1 125-139	L FOR FCA	0 159 160	H,K= 8, 0
9 219 218	L FOR FCA	0 68 -62	-2 154-165	-1 270-268	-8 253 249	3 105-102	0 234 207	4 114 114	-4 30 -31	0 43 -19	-9 198 200	2 35 -15	-10 25 19	2 93 -90	L FOR FCA
10 77 -70	0 44 -21	1 53 -50	0 150 332	-7 223 216	4 66 55		1 120-121	5 154-155	-2 98 -99	1 123-141	-8 5 5	3 60 57	-9 41 37		-4 35 -34
	1 302-301	2 50 -44	0 39 50	1 319 336	-6 199-197	5 71 68	2 7 -6	6 153-145	-2 34 34	-7 12 -22	4 26 34	-8 85 84	H,K= 7, 1	-6 71 70
H,K= 0, 3	2 19 17	3 90 87	1 23 32	2 115 -98	-5 146-144		3 92 -81		-1 106-107	3 171 176	-6 5 2	-7 125-132	L FOR FCA	-4 71 -78
L FOR FCA	3 24 86	4 102 90	2 22 21	3 231-229	-4 77 75	H,K= 2,10	4 148-147	H,K= 3, 8	0 31 13	4 112 109	-5 114-109	H,K= 6, 7	-6 159-155	-9 131-134	-2 40 20
1 39 -42	4 18	5 80 74	3 103 -99	4 114 108		L FOR FCA	6 194 193	FOR FCA	1 193 181	5 100 -94	1 38 -5	L FOR FCA	-5 101 104	-8 128 126	0 45 -8
2 23 -10		6 22 -7	4 42 -41	5 81 78	-2 129 128	-6 32 -32	6 190 188	-7 29 -29	2 46 21	6 56 -44	-3 292 305	-4 233 239	-7 115 106	
3 49 45	H,K= 0,11	7 25 13	5 53 51	6 29 -6	-1 166 169	-3 13 12	7 179-182	-6 61 -55	3 185-161		-2 22 -11	-6 19 -14	-3 38 -49	-6 68 -76	H,K= 8, 1
4 25 6	L FOR FCA	8 20 11	6 49 -46	7 74 69	0 248-247	-2 22 22	8 185-181	-4 38 47	4 162 149	H,K= 4, 7	-3 365-392	-5 11 -16	-2 56 -59	-5 28 -21	L FOR FCA
5 21 -9	1 56 -21	9 22 7	7 21 -4	8 89 -83	1 244-255	-1 51 -61		-4 105 113	5 94 87	L FOR FCA	0 38 6	-4 5 -2	1 11 3	-4 69 -67	-7 53 50
6 70 66		10 17 -4		9 82 -76	2 352 355	0 9 -11	H,K= 3, 4	-3 45 40	6 47 -37	-8 35 -29	1 247 268	-3 15 15	0 35 -16	-3 111-117	-7 61 -59
7 81 -75	H,K= 1, 0		H,K= 1, 8		3 200 204	1 82 62	L FOR FCA	-2 71 -70	7 23 -11	-7 81 97	2 38 -11	-2 81 -92	-4 90 56	-2 146 154	-4 107 109
8 78 -79	L FOR FCA	H,K= 1, 4	L FOR FCA	H,K= 2, 2	4 143-144	2 111-103	-10 186-180	H,K= 4, 3		-7 61 57	3 255-269	1 60 -55	4 44 -25	-1 178 154	-5 141 143
9 101 98	-10 35 31	L FOR FCA	-7 20 2	L FOR FCA	5 48 -47	3 82 -72	-9 5 10	0 52 42	H,K= 4, 3	-5 85 -91	4 44 29	0 30 8	3 64 -46	0 185-179	-4 146-157
10 175 162	-8 42 45	-10 44 -31	-6 100-104	-11 50 46	6 37 -21		-8 39 38	1 24 -16	L FOR FCA	-4 32 -29	5 122-123	1 60 -55	4 44 -25	1 163-158	-3 130-139
	-6 107-103	-9 24 19	-5 58 -62	-12 55 53	7 43 -28	H,K= 3, 0	-7 16 16	2 28 -5	-11 135-135	-3 80 87	6 33 8	2 34 -4		2 57 42	-2 83 83
H,K= 0, 4	-4 154 140	-8 25 -12	-4 134 127	-9 68 -59	8 68 66	L FOR FCA	-6 95 95	3 27 -26	-10 -23 -18			3 48 -43	H,K= 6, 6	3 99 83	-1 66 64
L FOR FCA	-2 369-364	-7 34 -24	-3 19 7	-8 207 197		-10 219 215	-5 21 -1	4 22 3	-9 12 5	H,K= 5, 3			L FOR FCA		0 57 -26
0 61 -22	0 154 134	-6 157 153	-2 210-197	-7 37 33	H,K= 2, 6	-8 67 -63	-4 185-180	5 29 -13	-8 57 53	L FOR FCA			-9 11 -11	H,K= 7, 2	1 53 21
1 10 1	2 234 230	-5 50 -51	-5 91 84	L FOR FCA	-4 172 171	-3 91 -91	2 195 200	H,K= 3, 9	-7 43 -38	H,K= 5, 8			-8 78 75	L FOR FCA	
2 319 323	4 331-337	-4 389-392	0 34 60	-5 4 4	-2 195 200		L FOR FCA	-6 28 -34	2 132-103	L FOR FCA			-7 17 10	-9 21 14	H,K= 8, 2
3 19 -9	6 589 633	-3 46 42	1 42 -27	-4 12 -23	-8 142 132	-2 92 -83	-1 37 -46	L FOR FCA	-5 81 78	3 167 168	-8 31 -37	-4 154-154	-5 27 33	-8 123-121	L FOR FCA
4 110-101	8 258-261	-2 256 242	2 135 132	-3 9 15	-7 33 -30	0 160 -66	0 69 -56	-6 48 -44	-4 109 93	4 77 83	-7 6 14	5 121-118	6 25 19	-7 9 13	-7 60 60
5 23 -2	10 45 -23	-1 7 5	3 24 15	-2 22 -7	-6 35 27	2 7 -16	1 66 -68	-5 112-110	-3 31 -38	5 121-118	-6 25 19		4 266 278	-6 52 -62	-6 18 -4
6 157-151		0 81 -74	4 221-220	-1 118-116	-5 16 -16	4 29 7	2 31 -11	-4 123 122	-2 28 -14		-5 47 48	-2 207 240	-3 32 -28	-5 22 -3	-5 87 -88
7 17 4	H,K= 1, 1	1 14 7	5 25 19	0 25 7	-4 27 35	6 62 -62	3 46 28	-3 124 126	-1 71 -68	H,K= 4, 8	-4 5 -8	0 300-341	-2 82 -92	-4 50 56	-4 25 -11
8 179 174	L FOR FCA	2 161-156	6 350 353	1 211 209	-3 3 8	8 67 56	4 24 -19	-2 114-115	0 144-135	L FOR FCA	-3 25 -28	1 30 -34	-3 51 -52	-3 53 58
9 27 -8	-11 109 104	3 15 11	7 20 -20	2 358-351	-2 40 -47		5 37 -31	-1 89-103	1 151 186	-7 23 -19	-2 33 27	1 30 12	0 112-112	-2 23 19	-2 119-113
10 234-231	-10 75 -73	4 369 374		3 199-189	-1 77 73	H,K= 3, 1	0 58 50	0 88 112	1 172 181	-6 337-338	-1 21 1	2 113 113	1 30 2	-1 119 120	-1 32 -12
	-9 24 -17	5 13 -2	H,K= 1, 9	4 64 51	0 79 69	1 58 47	7 29 -15	1 35 47	3 192-202	1 45 -13	0 44 -24		2 178 183	0 36 3	0 33 -11
H,K= 0, 5	-8 60 -51	6 113 -99	L FOR FCA	5 88 90	1 156-168	-11 104-102	8 85 -81	2 25 6	4 256-241	-4 142 136	3 39 -55	H,K= 5, 9	3 24 -27	1 146-139	
L FOR FCA	-7 136-122	7 8 1	-6 109 108	6 27 13	2 186-178	-10 61 59		3 64 56	5 140 136	-3 32 39	2 37 19	L FOR FCA	4 252-247	2 123 111	H,K= 8, 3
1 30 5	-6 65 -64	8 105 101	-5 103 94	7 85 -82	3 185 190	-9 83 77	H,K= 3, 5		6 98 97	-2 6 1	3 36 -4			3 90 76	L FOR FCA
2 50 52	-5 255 250	9 21 -5	-4 82 -81	8 29 11	4 30 -5	-8 39 -47	L FOR FCA	H,K= 3,10	7 42 -31	-1 23 -35	4 25 7	H,K= 6, 5			-6 78 77
3 31 14	-4 59 -40		-3 116-118	9 165-163	5 53 -45	-7 14 4	-10 124-116	L FOR FCA		0 87 -99	5 60 -48	L FOR FCA	H,K= 7, 3	-6 123 119	
4 45 -42	-3 269-261	H,K= 1, 5	-2 106 90		6 34 31	-6 94 -88	-9 64 -62	-4 33 -27	H,K= 4, 4	1 22 36	6 81 -75		-8 91 -92	L FOR FCA	-5 152-154
5 32 27	-2 230 227	L FOR FCA	-1 101 107	H,K= 2, 3	7 79 -69	-5 179-170	-8 51 46	-3 78 -66	L FOR FCA	2 42 12		H,K= 0, 0	-9 94 -97	-6 175 173	-4 153-165
6 47 -31	-1 152 153	-10 72 70	0 22 -6	L FOR FCA	8 13 2	-4 222 221	-7 42 -43	-2 90 88	-10 103 99	3 42 12	H,K= 5, 4	L FOR FCA	-6 146 147	-8 171 179	-3 159 159
7 84 -66	0 64 -52	-9 37 29	1 15 -15	-11 88 75		-3 257 258	-6 74 74	-1 40 45	-9 5 -9	4 70 -66	L FOR FCA	-10 23 13	-5 119 128	-7 154-153	-2 155 171
8 70 72	1 13 10	-3 48 47	2 30 -19	-10 162 156	H,K= 2, 7	-2 144-134	-9 165 146	0 20 27	-8 203-205		-10 256 253	-4 186-192	-6 100-103	-1 109-112
9 103 89	2 93 -88	-7 78 82	3 28 -14	-9 201-192	L FOR FCA	-4 229-234	1 25 -25	-7 5 -5	H,K= 4, 9		-9 128 -126	-2 226 217	-3 37 -41	0 63 -52
	3 90 -82	-6 189-185	4 56 54	-8 270-265	-8 136 126	0 233 196		-6 101 97	L FOR FCA		-8 96 -94	-4 144-143	-2 46 43	-4 21 -13	
H,K= 0, 6	4 74 72	-5 204-201	5 58 54	-7 178-165	1 100 96	-2 370 380	H,K= 4, 0	-5 11 7	-7 91 -72		-7 9 -2	-2 161 165	-1 23 5	-3 75 87	H,K= 8, 4
L FOR FCA	5 80 77	-4 354 354		-6 224 220	-6 144 140	1 239 254	L FOR FCA	-4 224-232	-5 54 52		0 30 -31	0 19 -20	-4 46 42	-2 126 127	L FOR FCA
0 27 12	6 96 -88	-3 218 204	H,K= 1,10	-5 177-166	-5 111 116	3 114 107	0 184-184	-10 106-105	-3 21 10	-1 6 -5	-6 5 3	2 228-231	1 41 30	-1 149-158	-6 83 -88
1 298 269	7 37 -30	-2 154-152	L FOR FCA	-4 42 47	4 171-171	1 80 -86	-8 346 330	-2 14 19	-2 18 -16	-4 187 194	4 213 222	2 39 -39	0 153-147	-5 24 2
2 14 -2	8 14 -85	1 100 96	-3 13 20	-3 37 39	5 139-120	2 16 13	6 585-607	-1 23 9	-9 18 -16	-4 5 -8		3 60 -39	1 123 120	-4 67 74
3 242-234	9 24 -3	0 34 14	-4 89 -82	-2 129-125	-7 98 95	6 219 219	1 69 -65	-4 206 198	0 192 196	0 43 -59	-2 286-335	H,K= 0, 1	2 114 122	2 39 -30	-3 26 -13
4 18 -11	10 29 2	1 15 6	-3 135-125	-1 239 239	-1 156-168	7 182 188	4 141 141	-2 21 22	1 30 -3	1 95-113	-1 9 5	L FOR FCA		3 44 -27	-2 66 -47
5 47 -32		2 71 69	-2 41 29	0 312 275	0 163-180	8 108-106	5 164 161	6 176-156	2 187-203	2 114 122	0 73 73	-10 23 -14	H,K= 6, 6		-1 8 13
6 22 6	H,K= 1, 2	3 76 71	-1 144 139	1 270-279	1 206 238		6 181-179	2 229 243	3 62 15		1 24 5	L FOR FCA	L FOR FCA		
7 151 142	L FOR FCA	4 106-102	0 32 -32	2 427-431	2 100 96		7 166-157	4 85 -80	4 197 198	H,K= 5, 0	2 86 -99	-8 105 102	-7 112-114	L FOR FCA	
8 24 -21	-11 37 32	5 47 -38	1 13 19	3 186 173	3 188-196	L FOR FCA		6 42 36	5 41 -24	L FOR FCA	3 38 4	-7 144 146	-6 30 -14	-8 9 -4	
9 200-189	-11C 17 5	6 17 7	3 41 18	4 165 166	4 93 -92	-11 192 180	H,K= 3, 6	8 27 -4	6 6C -50	-10 145-135	4 41 -26	-6 153-153	-5 187 196	-7 23 4	
	-9 22 -10	7 17 23	3 127-116	5 68 -56	5 30 31	-10 33 -38	L FOR FCA		7 37 -27	-8 232 253	5 38 2	-5 185-184	-4 71 72	-6 25 -29	

Table 3. *Distances and angles in* $ReCl_5$

Re(1)–Re(2)	3·739 ± 0·002 Å		
Re(1)–Cl(4)	2·223 ± 0·014	Re(2)–Cl(8)	2·223 ± 0·012 Å
Re(1)–Cl(2)	2·245 ± 0·012	Re(2)–Cl(9)	2·238 ± 0·013
Re(1)–Cl(10)	2·252 ± 0·013	Re(2)–Cl(5)	2·244 ± 0·012
Re(1)–Cl(7)	2·273 ± 0·014	Re(2)–Cl(3)	2·252 ± 0·012
Re(1)–Cl(1)	2·471 ± 0·011	Re(2)–Cl(6)	2·450 ± 0·011
Re(1)–Cl(6)	2·486 ± 0·011	Re(2)–Cl(1)	2·454 ± 0·011
Cl(1)–Re(1)–Cl(2)	87·3 ± 0·4°	Cl(1)–Re(2)–Cl(3)	90·3 ± 0·4°
Cl(1)–Re(1)–Cl(4)	91·0 ± 0·4	Cl(1)–Re(2)–Cl(5)	87·0 ± 0·4
Cl(1)–Re(1)–Cl(6)	80·8 ± 0·4	Cl(1)–Re(2)–Cl(6)	81·9 ± 0·4
Cl(1)–Re(1)–Cl(7)	172·2 ± 0·4	Cl(1)–Re(2)–Cl(8)	173·6 ± 0·4
Cl(1)–Re(1)–Cl(10)	86·5 ± 0·4	Cl(1)–Re(2)–Cl(9)	85·3 ± 0·4
Cl(2)–Re(1)–Cl(4)	93·8 ± 0·5	Cl(3)–Re(2)–Cl(5)	92·9 ± 0·4
Cl(2)–Re(1)–Cl(6)	85·6 ± 0·4	Cl(3)–Re(2)–Cl(6)	172·1 ± 0·4
Cl(2)–Re(1)–Cl(7)	93·0 ± 0·5	Cl(3)–Re(2)–Cl(8)	96·1 ± 0·4
Cl(2)–Re(1)–Cl(10)	170·4 ± 0·4	Cl(3)–Re(2)–Cl(9)	92·8 ± 0·4
Cl(4)–Re(1)–Cl(6)	171·9 ± 0·4	Cl(5)–Re(2)–Cl(6)	85·8 ± 0·4
Cl(4)–Re(1)–Cl(7)	96·7 ± 0·5	Cl(5)–Re(2)–Cl(8)	92·7 ± 0·4
Cl(4)–Re(1)–Cl(10)	93·6 ± 0·5	Cl(5)–Re(2)–Cl(9)	170·4 ± 0·4
Cl(6)–Re(1)–Cl(7)	91·4 ± 0·4	Cl(6)–Re(2)–Cl(8)	91·7 ± 0·4
Cl(6)–Re(1)–Cl(10)	86·2 ± 0·4	Cl(6)–Re(2)–Cl(9)	87·5 ± 0·4
Cl(7)–Re(1)–Cl(10)	92·2 ± 0·5	Cl(8)–Re(2)–Cl(9)	94·4 ± 0·4

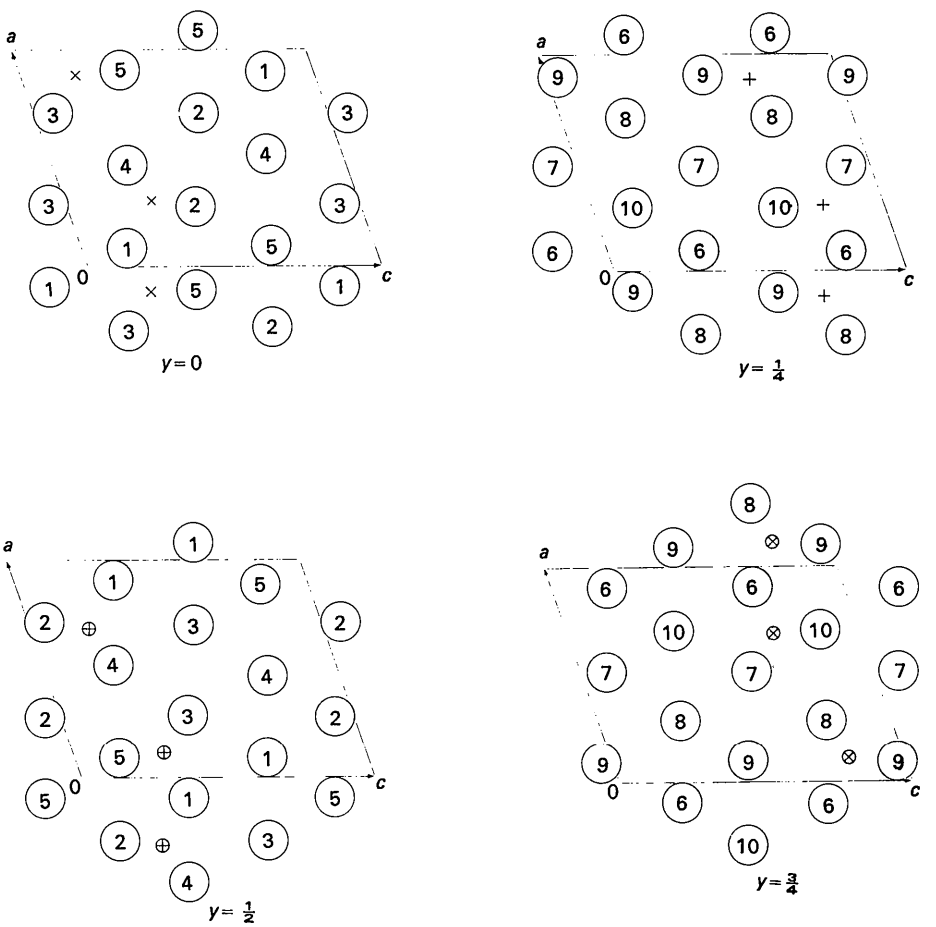

Fig. 2. Sequence of networks along the *b* axis. Chlorine positions are based on a double-hexagonal closest packing arrangement; rhenium atoms at $y = \pm\frac{1}{8}$ and $\pm\frac{3}{8}$ occupy octahedral holes between layers. The various chlorine atoms are indicated by numbers. Re atoms at $\frac{1}{8}$ and $-\frac{1}{8}$ are indicated by × and ⊗ respectively; Re at $\frac{3}{8}$ and $-\frac{3}{8}$ by + and ⊕ respectively.

might be expected, *cf.* Re^{IV}–Cl distances of (*a*) 2·35 ± 0·02 Å in bis-[*p*-toluidinium] hexachlororhenate (Adman & Margulis, 1967) and (*b*) 2·38 ± 0·02 Å in $K_4[ReOCl_5]_2 . H_2O$ (Morrow, 1962). In contradistinction, the present Re–Cl distances involving nonbridging Cl are (reasonably enough) shorter than the Re^{IV}–Cl distances cited above.

The rhenium atoms are both shifted by about 0·20 Å from the centers of the octahedra in directions *away* from one another, *i.e.* along the line joining Re(1) and Re(2) (Fig. 1). Again, displacements of a similar magnitude are observed in the other bridged-dimer pentahalides, and suggest a strong repulsion, presumably of a coulombic nature, between metal atoms. As a result of this distortion, bond angles within the octahedra deviate noticeably from 90°, although the Cl···Cl distances outlining the octahedra are rather constant at 3·27 ± 0·05 Å. The angles deviating most drastically from 90° are Cl(1)–Re(1)–Cl(6) = 80·8° and Cl(1)–Re(2)–Cl(6) = 81·9°.

The crystal structure as a whole is based on a double-hexagonal closest packing (d.h.c.p.) of Cl atoms, in which Re atoms occupy one-fifth of the octahedral holes. This arrangement is illustrated in Fig. 2 where the four hexagonal nets characteristic of d.h.c.p. are shown. The stacking sequence of these nets along the *b* axis is *ABAC*... For the present arrangement of Re atoms and for the idealized case of exact d.h.c.p. of Cl atoms, simple geometrical considerations require that the repeat distance along the *b* axis be $4\sqrt{8/3}R$, (R = the packing radius of Cl). Similarly, the *a*- and *c*-axis repeat distances are related to distances within the hexagonal nets as follows: $a = 2\sqrt{7}R$, $c = 4\sqrt{3}R$; the monoclinic angle is $90 + (\sqrt{3}/2\sqrt{7})$ (= 109·1°). Numerical values for $R = 1{\cdot}75$ Å are: $a = 9{\cdot}26$, $b = 11{\cdot}43$ and $c = 12{\cdot}12$ Å, compared with experimental values of $a = 9{\cdot}24$, $b = 11{\cdot}54$ and $c = 12{\cdot}03$; $\beta = 109{\cdot}1°$. The use of a more conventional value of $R = 1{\cdot}80$ Å (Pauling, 1960) leads to predicted repeat-distances which are 2–4% larger than observed. As mentioned earlier, the intra-octahedral Cl···Cl distances average well below 3·60 Å, so that a smaller overall Cl packing radius is to be expected.

This d.h.c.p. packing of Cl in $ReCl_5$ provides an interesting comparison with the behavior of Cl in the other bridged-dimer pentachlorides. In $NbCl_5$, $MoCl_5$ and $TaCl_5$, the Cl are in hexagonal closest packing (h.c.p.), and in UCl_5 the Cl are in cubic closest packing (c.c.p.). Thus, $ReCl_5$, $NbCl_5$ and UCl_5 represent three crystallographically distinct ways of forming M_2Cl_{10} dimers in the solid state. We note further that examples of these three packing modes are found in crystal structures of the rare-earth metals (Pauling, 1960). Samarium forms a still more complicated closest-packing arrangement which repeats after nine layers (Daane, Rundle, Smith & Spedding, 1954). It is inviting to speculate whether some of the pentahalides might display a halide atom arrangement of the Sm type.

It is relevant also to speculate on the possibility of the pentachlorides undergoing polymorphic transformations from one type of Cl packing to another. In the case of the rare-earth metals, Jayaraman & Sherwood (1964) indicate that with increasing pressure the transitions proceed in the order: h.c.p. → Sm-type → d.h.c.p. → f.c.c. There is no change in the number of nearest neighbors, but each step is accompanied by a small increase in density, or equivalently, a small decrease in the atomic volume. It is conceivable that this order originates from more favorable relations of second (and more distant) nearest neighbors, and that the sequence will be retained in other close-packed compounds. However, a comparison of structural data for $TaCl_5$, $ReCl_5$ and UCl_5 (Table 4) shows $ReCl_5$ to possess far and away the highest density and lowest value of V_{Cl} (volume of unit cell/number of Cl atoms within the unit cell). In this respect the effect of Re

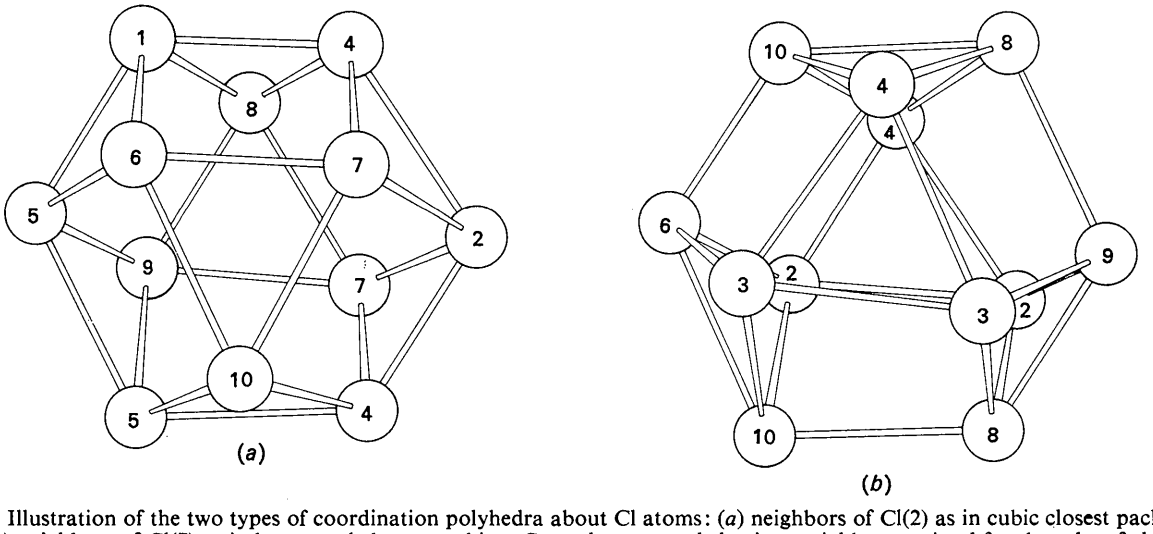

Fig. 3. Illustration of the two types of coordination polyhedra about Cl atoms: (*a*) neighbors of Cl(2) as in cubic closest packing, and (*b*) neighbors of Cl(7) as in hexagonal closest packing. Central atoms and rhenium neighbors omitted for the sake of clarity.

is to cause a net compression of the Cl framework. This would seem analogous to an external mechanical pressure. The higher density for UCl_5 than for $TaCl_5$ reflects a heavier mass; actually of the three, UCl_5 has the most open structure. The data in Table 4 therefore suggest that UCl_5 or $TaCl_5$ may transform under pressure to the d.h.c.p. arrangement; conversely at higher temperatures $ReCl_5$ or $TaCl_5$ may transform to the c.c.p. arrangement.

Table 4. *Comparison of structural data for the bridged-dimer pentachlorides*

V_{Cl} = volume of unit cell/number of Cl atoms within unit cell.

	$TaCl_5$	$ReCl_5$	UCl_5
Packing of Cl	h.c.p.	d.h.c.p.	c.c.p.
Density, g.cm^{-3}	3·68	3·98	3·81
V_{Cl} (Å^3)	32·3	30·3	36·2
M–Cl (bridge) (Å)	2·56*	2·47	2·69
M–Cl (nonbridge) (Å)	2·28*	2·24	2·44
M...M (dimer) (Å)	3·95*	3·74	4·17

* Estimated from positional parameters for $NbCl_5$.

In $ReCl_5$, half of the Cl atoms [Cl(1) through Cl(5)] have their 12 Cl neighbors arranged as in c.c.p., and the other half [Cl(6) through Cl(10)] have their neighbors arranged as in h.c.p. The polyhedra are not in general regular, since contacts between Cl atoms within the same octahedron are smaller than contacts between Cl in different dimers. In addition to having 12 Cl neighbors, every Cl atom is bonded to at least one Re; Cl(1) and Cl(6) are bonded to two Re atoms. A complete list of nearest neighlor Cl···Cl distances is given in Table 5. A typical coordination polyhedron of each type is illustrated in Fig. 3; the others can be constructed by overlaying the networks of Fig. 2.

Table 5. *Nearest neighbor* Cl(*i*)–Cl(*j*) *distances in* $ReCl_5$

Distances (Å) given for $j \geq i$.
Intra-octahedral distances indicated by asterisks.

i j	*d*	*i j*	*d*	*i j*	*d*
1–1	3·67	2–9	3·69	5–6	3·74
–2	3·26*	–10	3·70	–8	3·23*
–3	3·34*	3–3	3·67	–9	3·66
–3	3·73	–4	3·65	–9	3·77
–4	3·35*	–4	3·65	–10	3·75
–5	3·24*	–5	3·26*	6–7	3·41*
–6	3·21*	–6	3·64	–8	3·36*
–6	3·65	–7	3·61	–9	3·24*
–8	3·65	–7	3·65	–9	3·66
–9	3·18*	–8	3·32*	–10	3·24*
–9	3·74	–9	3·25*	–10	3·71
–10	3·24*	–10	3·73	7–8	3·58
2–2	3·81	4–5	3·74	–8	3·62
4	3·26*	–7	3·75	–9	3·66
4	3·62	–7	3·36*	–10	3·26*
5	3·33	–8	3·48	–10	3·65
5	3·58	–8	3·65	8–9	3·27*
6	3·22*	–10	3·26*	–9	3·63
7	3·28*	–10	3·72	–10	3·66
7	3·72	5–5	3·64	9–10	3·40
8	3·68	–6	3·20*		

Standard deviations in the *d*'s = 0·02 Å.

As pointed out previously for UCl_5 (Smith, Johnson & Elson, 1967), a description of the structure in terms of a closest-packed array leaves open the question whether the M_2Cl_{10} dimers have an independent existence as discrete molecules. We know of no information relating to whether or not the Re_2Cl_{10} dimers are retained in the liquid or vapor phase or upon dissolution of $ReCl_5$ in an inert solvent.

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