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Direct Determination of the Crystal Structure of $PaOCl_2$*

BY RICHARD P. DODGE,† GORDON S. SMITH, QUINTIN JOHNSON AND ROBERT E. ELSON
Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

(*Received* 12 *June* 1967)

A compound obtained during a reduction of $PaCl_5$ has been studied by single-crystal X-ray diffraction techniques and identified as the oxydichloride, $PaOCl_2$. Crystals of this material are orthorhombic with $a=15{\cdot}25$, $b=17{\cdot}86$, $c=4{\cdot}01$ Å. The space group is *Pbam*, and the unit cell contains twelve $PaOCl_2$ units. Phase determination was by means of the symbolic addition procedure; full-matrix least-squares refinement of diffractometrically measured data resulted in a final *R* index of 7·6%. The structure consists of infinite polymeric chains which extend along the short *c* axis and which are cross-linked to one another in the *ab* plane by bridging Cl atoms. The repeating unit of structure along the chain is the twelve-atom aggregate, $Pa_3O_3Cl_6$. The Pa atoms are seven-, eight- and nine-coordinated. The oxygen atoms are three- and four-coordinated; the chlorine atoms, two- and three-coordinated. Pa–O and Pa–Cl bond distances are in the respective ranges 2·19–2·38 Å and 2·74–3·08 Å.

Introduction

During the course of preparing protactinium tetrachloride by hydrogen reduction of the pentachloride, we encountered crystals quite unlike those of the expected product. It appeared likely that the unknown phase was a second modification of $PaCl_4$ or possibly a chloride of mixed oxidation states, *e.g.* Pa_2Cl_9. A crystal-structure determination shows the phase instead to be a complex oxychloride of empirical composition $PaOCl_2$.

We may mention that solution of the crystal structure was effected by the symbolic addition procedure. Prior to that, an attempt by conventional Patterson analysis had been unsuccessful. In retrospect, the lack of success with the latter approach is traceable to a serious misestimate of the number of Pa atoms within the unit cell. On the other hand, this misestimate proved of no handicap in the symbolic addition procedure.

Experimental

Our sample of protactinium, in the form of $PaO_{2\cdot25}$, was received from Oak Ridge National Laboratory. This sample, originally part of a gram-scale lot recovered by investigators at the Atomic Energy Research Establishment, Harwell, England, is now known to contain about 4% Nb [for further details see Stein (1964)]. Preparation of the samples followed lines previously described (Elson, Fried, Sellers & Zachariasen, 1950). $PaO_{2\cdot25}$ was treated with carbon tetrachloride at about 200°C to produce $PaCl_5$ as well as a less volatile component (probably oxychlorides of Pa^V). Following fractional sublimation, the pentachloride was reacted with hydrogen at 800°C. Unreacted pentachloride was separated from the less volatile tetra-

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Permanent address: Chemistry Department, University of the Pacific, Stockton, California.

chloride by fractional sublimation. $PaCl_4$ was sublimed into thin-walled glass capillaries. These capillaries were filled with hydrogen, sealed off, and then placed in a thermal gradient to promote the growth of single crystals. These capillaries served to protect the samples against the hydrolytic effects of moisture as well as to protect personnel from radioactive hazards (^{231}Pa, the isotope used, is an α-emitter).

Despite precautions, at least part of the product obtained proved ultimately to be an oxychloride. It may well be that trace amounts of moisture in the hydrogen gas caused an accidental hydrolysis of $PaCl_4$. Alternatively, an oxychloride of Pa^V may have been carried along in the fractional separations. Conceivably, this material could have been converted to $PaOCl_2$ by reduction. Our syntheses typically involve 0·1 mg of $PaO_{2\cdot25}$ so that side reactions due to traces of moisture become relatively important. Moreover, our experimental techniques were conducive to the detection of minute amounts of products that might otherwise go unnoticed in larger preparations. For example, the entire diffraction record came from a crystal weighing approximately 0·10 microgram.

Microscopic examination of one sample tube showed a cluster of orange crystals. One thin blade-like crystal measuring about $0{\cdot}02\times0{\cdot}002\times0{\cdot}35$ mm had apparently broken off this cluster and was adhering to the capillary wall, well separated from the others. This specimen was examined further by X-rays on a General Electric XRD-5 diffractometer equipped with a goniostat. The crystal class proved to be orthorhombic rather than tetragonal as reported for $PaCl_4$ (Elson *et al.*, 1950). The systematic extinctions (0*kl*, *k* odd; *h*0*l*, *h* odd) are characteristic of the space groups *Pbam* and *Pba*2 (*International Tables for X-ray Crystallography*, 1952). Refined values of the lattice constants based on Mo $K\alpha=0{\cdot}7107$ Å are: $a=15{\cdot}25$, $b=17{\cdot}86$, $c=4{\cdot}01$ Å (with probable errors of 0·3%). Oscillation and Weissenberg photographs indicated the crystal would be suitable for intensity purposes.

Intensity measurements were carried out by the stationary-crystal, stationary-counter technique (Furnas, 1957). The radiation used was Zr-filtered Mo $K\alpha$. In all, 610 reflections were recorded up to a 2θ-cutoff of 40°. The intensities were reduced to relative $|F|$'s through the application of Lorentz–polarization factors.

Determination of the structure

That the orthorhombic phase was a second form of $PaCl_4$ received support from volume and density considerations. In closest packing, each chlorine atom requires about 34 Å^3. From this the number of chlorine atoms indicated within the unit cell was 32. For eight molecules of $PaCl_4$ per unit cell, the calculated density was 4·53 g.cm^{-3}, a value only 4% smaller than the calculated density for tetragonal $PaCl_4$ (Elson *et al.*, 1950). It also appeared reasonably certain that the z coordinates of the atoms could only be 0 and $\frac{1}{2}$. This followed from the observation of an exceptionally strong 002 reflection, as well as from packing restraints imposed by the short c axis (4·01 Å).

The Patterson function was far more complex than expected. The peaks were indeed heavily concentrated at levels of $W=0$ and $\frac{1}{2}$; however, no satisfactory interpretation could be obtained for an ordered arrangement of eight heavy atoms. A solution in terms of a disordered structure was pursued briefly, but again without success.

At this point, phase determination by means of the symbolic addition procedure (see, *e.g.* Karle & Karle, 1965) was tried. Prof. H. L. Ammon kindly supplied a copy of his PHASER program for this purpose. Operational aspects and general strategy of the PHASER program have been described by Ammon & Sundaralingam (1966). Conversion of intensity data to $|E(hkl)|$ values and their sorting with regard to magnitude and parity of Miller indices was accomplished through the use of J. M. Stewart's X-ray 63 library of programs.

The symbolic addition procedure was carried out on the 109 reflections having $|E|$'s greater than 1·3. Origin determining signs were chosen for the 8,11,1, 8,7,2 and 1,10,3 reflections as +, − and +, respectively. (In using this direct method, we assumed the structure to be centrosymmetric.) It also appeared likely that the sign of 002 was + (as would be expected for a heavy concentration of atoms at $z=0$ and $\frac{1}{2}$) and that 870 had the same sign as 872, namely −. One additional reflection, 2,13,1, was given a symbolic sign. A pass through PHASER produced a consistent set of signs for a phase angle of π for 2,13,1. Of the 109 signs determined, all agreed with our final structure factor calculation.

A Fourier synthesis with these E's as coefficients showed, to our surprise, twelve Pa peaks rather than eight as heretofore expected. Vector interactions between these atoms gave good agreement with the observed Patterson map. An R index of 27% for the structure factor calculation convinced us further of the essential correctness of the model. Conventional 'heavy-atom' techniques were used to locate first the chlorine atoms and then the oxygen atoms. Difference maps gave residual features around Pa sites, and anisotropic temperature factors for Pa were used in subsequent refinements.

Is is quite clear that the difficulty we experienced in interpreting the Patterson map was due to a strong predilection for eight Pa atoms per unit cell. As mentioned, the evidence for this, while indirect, was persuasive. We note that this same assumption went into the direct-method approach. That is to say, E values were computed on the basis of there being eight $PaCl_4$ molecules per unit cell. As the cell actually contains twelve $PaOCl_2$ units, the derived E values were not correct. Nevertheless, phase determination by the symbolic addition procedure was perfectly straightforward. Our experience here suggests that the symbolic addition procedure, in conjunction with 'heavy-atom' techniques, could be applied with success to materials whose unit cell contents are only approximately known. This would be of particular value in the case of minerals and intermetallic compounds.

The structure model was refined by the full-matrix least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished). Pa atoms were given anisotropic temperature parameters; the others, isotropic thermal parameters. Atomic scattering factors for Pa were Hartree–Fock–Slater values of Hanson, Hermann, Lea & Skillman (1964), corrected for anomalous dispersion (Cromer, 1965); scattering factors for Cl^- and O were those listed in *International Tables for X-ray Crystallography* (1962). The refinement was based on $|F|$ with the following weighting scheme (Smith, Johnson & Nordine, 1965): $w=F_o^{1/4}, F_o<A$; $w=A^{5/4}F_o^{-1}, F_o>A$. On the scale of the structure factor data of Table 1, A is 360. Six cycles of refinement reduced the conventional R index to 7·6% (all reflections). Changes in the parameters at this stage were <0·001 times the standard deviations. Parameters from the last cycle were accepted as final, and are given in Table 2. (A refinement series was carried out in terms of the non-centrosymmetric space group *Pba*2, *i.e.* all z parameters, save one, were also allowed to vary. With this additional freedom, the z parameters tended to oscillate near their values in *Pbam*, and convergence was slow. After seven cycles the R index decreased to 7·3%. Differences between the x and y coordinates from those obtained in *Pbam* were negligible. For nine

Table 1. *Observed and calculated structure factors*

H,L=	K	FOBS	FCAL
0, 0	2	203	-191
	4	369	365
	6	40	-3
	8	216	206
	10	321	-322
	12	307	309
	14	351	-347
	16	168	-151
0, 1	0	410	-390
	2	138	-136
	4	504	-481
	6	419	410
	8	491	-483
	10	58	-13
	12	63	26
	14	200	208
	16	88	-85
0, 2	0	1031	1028
	2	162	-148
	4	339	298
	6	36	32
	8	187	177
	10	288	-279
	12	274	276
	14	298	-311
0, 3	0	260	-253
	2	115	-91
	4	423	-393
	6	304	297
	8	359	-354
	10	47	8
0, 4	0	642	638
1, 0	1	7	22
	2	364	-333
	3	256	-234
	4	73	57
	5	59	10
	6	177	-169
	7	60	17
	8	461	-453
	9	163	-148
	10	91	-79
	11	138	129
	12	149	-147
	13	130	124
	14	308	-335
	15	91	-63
	16	33	32
	17	42	5
1, 1	1	93	94
	2	97	-109
	3	204	-202
	4	376	369
	5	205	201
	6	187	194
	7	74	86
	8	97	96
	9	43	-17
	10	378	382
	11	64	-25
	12	173	186
	13	51	48
	14	44	14
	15	129	-137
	16	187	199
1, 2	1	23	19
	2	287	-259
	3	195	-179
	4	52	42
	5	25	10
	6	149	-148
	7	42	24
	8	362	-376
	9	130	-129
	10	74	-68
	11	123	108
	12	136	-134
	13	119	105
	14	276	-299
1, 3	1	92	79
	2	88	-78
	3	142	-122
	4	294	263
	5	150	130
	6	153	151
	7	59	62
	8	64	59
	9	52	-26
	10	282	299
2, 0	0	526	-540
	1	9	32
	2	87	-86
	3	234	-212
	4	309	-299
	5	485	463
	6	169	-159
	7	459	-433
	8	156	-144
	9	307	294
	10	200	199
	11	112	117
	12	142	-133
	13	145	137
	14	212	226
	15	149	-144
	16	90	93
	17	288	312
2, 1	0	255	287
	1	462	-468
	2	99	105
	3	26	48
	4	407	409
	5	78	-77
	6	15	-34
	7	58	-65
	8	228	222
	9	334	-330
	10	67	-35
	11	255	266
	12	67	-63
	13	398	-401
	14	118	-121
	15	170	162
	16	53	-55
2, 2	0	410	-421
	1	17	27
	2	71	-62
	3	189	-169
	4	233	-240
	5	400	397
	6	139	-127
	7	347	-344
	8	141	-123
	9	267	254
	10	168	165
	11	103	97
	12	124	-115
	13	126	118
	14	193	202
2, 3	0	183	203
	1	350	-333
	2	98	89
	3	89	72
	4	309	294
	5	92	-57
	6	38	-36
	7	63	-47
	8	167	168
	9	252	-254
	10	41	-31
3, 0	1	25	22
	2	15	8
	3	404	402
	4	140	120
	5	144	127
	6	331	310
	7	199	-186
	8	217	197
	9	307	303
	10	264	260
	11	222	-214
	12	105	93
	13	111	-101
	14	86	83
	15	100	79
	16	96	105
3, 1	1	220	-232
	2	13	-1
	3	123	129
	4	20	22
	5	271	-270
	6	130	-137
	7	178	-178
	8	275	-277
	9	204	192
	10	143	-137
	11	74	-47
	12	157	-157
	13	123	-102
	14	170	-163
	15	224	246
	16	86	-93
3, 2	1	17	18
	2	17	10
	3	344	324
	4	111	108
	5	85	79
	6	239	233
	7	147	-144
	8	167	160
	9	257	259
	10	228	223
	11	184	-181
	12	98	91
	13	90	-92
	14	72	76
3, 3	1	193	-183
	2	56	-29
	3	119	98
	4	43	-10
	5	189	-192
	6	102	-113
	7	141	-130
	8	200	-202
	9	147	142
	10	120	-111
4, 0	0	193	-210
	1	46	-59
	2	389	393
	3	74	65
	4	143	102
	5	574	-545
	6	122	104
	7	234	212
	8	67	19
	9	294	-276
	10	198	189
	11	84	-71
	12	275	-262
	13	236	-219
	14	112	95
	15	51	34
	16	108	-105
4, 1	0	120	-135
	1	405	420
	2	321	-333
	3	46	-70
	4	141	141
	5	217	217
	6	487	-468
	7	102	92
	8	178	166
	9	268	266
	10	38	22
	11	169	-166
	12	59	-9
	13	395	391
	14	67	59
	15	52	18
4, 2	0	144	-160
	1	46	-53
	2	324	332
	3	74	68
	4	83	81
	5	441	-445
	6	81	83
	7	179	175
	8	45	13
	9	255	-245
	10	179	169
	11	96	-65
	12	228	-234
	13	199	-191
4, 3	0	111	-113
	1	301	301
	2	224	-224
	3	78	-65
	4	107	95
	5	167	152
	6	337	-340
	7	72	70
	8	130	125
	9	219	220
5, 0	1	87	-94
	2	54	22
	3	248	-266
	4	365	-389
	5	148	-132
	6	104	-90
	7	102	-83
	8	114	110
	9	63	-63
	10	274	-259
	11	68	10
	12	148	-142
	13	68	55
	14	100	91
	15	86	66
	16	198	-202
5, 1	1	216	245
	2	356	365
	3	170	181
	4	141	-149
	5	185	192
	6	38	50
	7	74	65
	8	211	204
	9	83	-63
	10	65	-44
	11	41	-35
	12	120	118
	13	76	-33
	14	251	249
	15	118	-121
5, 2	1	109	-99
	2	41	52
	3	215	-216
	4	315	-306
	5	105	-108
	6	76	-78
	7	83	-67
	8	99	91
	9	90	-54
	10	228	-227
	11	50	12
	12	124	-127
	13	71	52
5, 3	1	175	176
	2	244	245
	3	116	121
	4	111	-104
	5	146	138
	6	60	49
	7	70	58
	8	165	172
	9	34	-39
6, 0	0	331	352
	1	149	179
	2	493	-493
	3	99	67
	4	105	98
	5	105	108
	6	80	-62
	7	276	266
	8	86	83
	9	193	173
	10	273	-261
	11	187	185
	12	380	345
	13	144	127
	14	187	-173
	15	135	132
6, 1	0	63	88
	1	74	106
	2	195	203
	3	107	-116
	4	296	-308
	5	129	-140
	6	481	470
	7	126	-117
	8	255	-235
	9	145	-141
	10	95	91
	11	297	-284
	12	38	-14
	13	67	-68
	14	77	65
	15	116	-111
6, 2	0	277	301
	1	131	133
	2	399	-404
	3	83	66
	4	77	77
	5	88	81
	6	72	-53
	7	243	232
	8	101	73
	9	167	150
	10	233	-236
	11	172	161
	12	313	308
6, 3	0	67	63
	1	80	70
	2	158	158
	3	59	-85
	4	227	-227
	5	110	-115
	6	358	359
	7	91	-93
	8	192	-190
7, 0	1	239	269
	2	69	-67
	3	43	-8
	4	113	101
	5	187	195
	6	25	11
	7	278	250
	8	113	-103
	9	110	-97
	10	126	124
	11	86	70
	12	75	58
	13	67	-50
	14	96	-46
	15	220	-223
7, 1	1	104	-129
	2	127	-142
	3	394	-404
	4	25	24
	5	18	6
	6	18	25
	7	60	-68
	8	176	-176
	9	144	-135
	10	96	89
	11	78	64
	12	80	-59
	13	233	236
	14	75	-82
7, 2	1	232	234
	2	55	-64
	3	20	-2
	4	90	91
	5	176	170
	6	29	12
	7	222	214
	8	97	-85
	9	104	-94
	10	97	109
	11	77	61
	12	63	52
7, 3	1	82	-92
	2	97	-101
	3	316	-302
	4	33	26
	5	23	-4
	6	24	14
	7	34	-51
8, 0	0	108	-83
	1	38	2
	2	29	37
	3	235	-245
	4	30	22
	5	231	240
	6	100	107
	7	489	-485
	8	107	-90
	9	54	-34
	10	51	0
	11	183	-171
	12	118	-98
	13	134	-127
	14	95	80
8, 1	0	149	152
	1	277	-304
	2	31	18
	3	240	235
	4	18	12
	5	144	153
	6	121	-128
	7	171	190
	8	35	40
	9	36	-8
	10	57	-42
	11	512	483
	12	51	51
	13	180	-178
8, 2	0	70	-71
	1	20	-1
	2	57	33
	3	226	-219
	4	41	10
	5	210	207
	6	96	88
	7	408	-429
	8	77	-76
	9	39	-28
	10	23	7
	11	149	-153
8, 3	0	81	101
	1	233	-236
	2	23	1
	3	193	185
	4	24	16
	5	120	114
9, 0	1	265	-298
	2	26	-23
	3	48	-22
	4	110	96
	5	178	-162
	6	85	82
	7	129	-114
	8	142	-114
	9	140	125
	10	162	150
	11	89	-77
	12	23	19
	13	24	-12
9, 1	1	98	99
	2	100	-115
	3	320	323
	4	27	49
	5	28	-1
	6	20	-3
	7	21	-19
	8	99	-91
	9	150	149
	10	50	44
	11	23	3
	12	53	-45
9, 2	1	251	-255
	2	21	-24
	3	30	-18
	4	105	84
	5	143	-144
	6	70	69
	7	108	-106
	8	95	-97
	9	117	114
	10	129	131
9, 3	1	54	76
	2	59	-90
10, 0	0	278	-275
	1	63	-64
	2	263	279
	3	116	119
	4	28	24
	5	63	-70
	6	29	18
	7	293	286
	8	37	-23
	9	49	10
	10	164	142
	11	158	148
	12	258	-233
10, 1	0	63	-43
	1	205	230
	2	102	-107
	3	206	-230
	4	134	138
	5	55	-68
	6	306	-314
	7	235	-239
	8	151	150
	9	22	-14
	10	23	-7
	11	232	-215
10, 2	0	231	-238
	1	44	-54
	2	245	246
	3	119	116
	4	32	19
	5	60	-62
	6	23	15
	7	271	256
	8	24	-21
11, 0	1	99	112
	2	152	170
	3	131	131
	4	180	-162
	5	63	84
	6	43	-47
	7	31	8
	8	22	24
	9	79	74
	10	161	-157
	11	41	-30
11, 1	1	137	-135
	2	120	141
	3	56	-64
	4	77	-86
	5	110	-114
	6	101	101
	7	22	-22
	8	211	212
	9	33	-33
	10	24	-37
11, 2	1	102	99
	2	135	147
	3	113	115
	4	161	-146
	5	74	75
	6	34	-43
	7	15	9
12, 0	0	160	135
	1	70	82
	2	251	-250
	3	30	-7
	4	75	-59
	5	163	-153
	6	105	-85
	7	51	40
	8	73	77
	9	155	-146
12, 1	0	22	-7
	1	116	115
	2	154	150
	3	22	-6
	4	92	-91
	5	23	-3
	6	314	303
	7	109	115
	8	136	-137
12, 2	0	129	121
	1	63	71
	2	230	-225
	3	24	-8
	4	54	-47
13, 0	1	22	24
	2	50	40
	3	150	-144
	4	114	111
	5	23	-15
	6	62	48
	7	58	46
13, 1	1	143	140
	2	65	-79
	3	57	-57
	4	81	-100
	5	108	98
	6	41	-20
14, 0	0	165	147
	1	33	52
	2	94	80
	3	88	-90
	4	24	25
	5	296	257
14, 1	0	90	-91
	1	221	-201
	2	115	-109

of the twelve independent atoms, z parameters were within 1·5σ of values in *Pbam*; z parameters for the other three atoms [Pa(2), Cl(5) and Cl(6)] deviated by 3–7σ. Whether this represents a significant departure from centrosymmetry for the structure as a whole is problematical. In view of suspected systematic errors in the intensity data, as well as somewhat limited resolution along the c axis, we feel it is justifiable to ignore the lower R index obtained in *Pba*2. Grosser features of the structure are, of course, unaltered, whichever space group is adopted.)

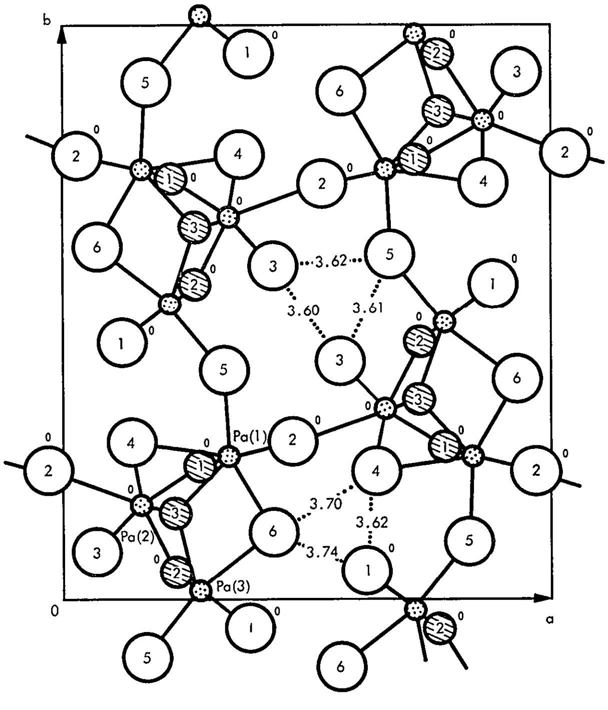

Fig. 1. Projection of structure on (001). Infinite polymeric chains, $(Pa_3O_3Cl_6)_n$, run normal to page. Open circles represent Cl atoms; stippling and stripes in circles indicate Pa and O atoms, respectively. Atoms at $z=0$ are indicated by small zeroes; the remaining atoms are at $z=\frac{1}{2}$.

There appears to be a small, but definite, trend in our data in that for weak reflections the observed structure amplitudes are generally larger than the calculated values. A number of possible explanations can be advanced: background levels somewhat underestimated, uncertainties in the scattering factors for Pa, or incorporation of contaminant Nb into Pa sites. None were explored further. The fairly pronounced anisotropy of thermal vibration for Pa atoms (all have large B_{11} terms) probably reflects these deficiencies. The absorption coefficient of $PaOCl_2$ is calculated to be 512 cm^{-1} for Mo $K\alpha$ radiation; hence absorption errors may also be responsible in part for the observed anisotropy.

Despite these reservations, the intensity data sufficed to locate the unsuspected oxygen atoms in a straightforward way. These atoms were readily apparent in a difference synthesis (after the Pa/Cl ratio was established as 1:2) as peaks about one-half as high as those for Cl atoms, and moreover were quite well-behaved during least-squares refinement. A structure-factor calculation with the oxygen atoms removed, but with Pa and Cl at their final positions, gave an R value of 9·9%. Comparison of this with the final R of 7·6% illustrates the overall contribution of oxygen to the structure factors. A final difference map shows some residual features which occasionally amount to ± 2 e.Å^{-3}, but which, however, are diffuse, irregular, or impossibly close to atomic sites.

At the time our structural analysis was completed, we could find no account of $PaOCl_2$ in the literature. Hence, identification of the small peaks as oxygen (rather than, say, nitrogen or fluorine) and specifically as oxide oxygen (rather than OH$^-$ or H_2O) followed from chemical intuition. Quite recently, Dr D. Brown has kindly furnished us with a preprint (Brown & Jones, 1967) describing the preparation and properties of $PaOCl_2$. Of especial interest is the fact that the powder pattern data given for their preparation are satisfactorily accounted for by the present structure. Dr Brown also reports that the oxydichlorides of Th, Pa, U and Np are all isostructural with one another.

Table 2. *Final parameters*

E.s.d.'s in parentheses. Anisotropic temperature factor expressed as:
$\exp\left[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*)\right]$.
Units of B or B_{ij} are Å^2.

	$10^4\,x$	$10^4\,y$	z	B or B_{11}	B_{22}	B_{33}	B_{12}
Pa(1)	3372 (2)	2480 (1)	$\frac{1}{2}$	2·6 (0·1)	0·9 (0·1)	0·3 (0·1)	−0·2 (0·1)
Pa(2)	1566 (2)	1656 (1)	0	2·5 (0·1)	0·6 (0·1)	0·4 (0·1)	−0·1 (0·1)
Pa(3)	2815 (2)	248 (1)	$\frac{1}{2}$	3·1 (0·1)	0·4 (0·1)	0·4 (0·1)	0·2 (0·1)
Cl(1)	1206 (13)	4510 (10)	0	2·6 (0·4)			
Cl(2)	4711 (12)	2819 (10)	0	1·8 (0·4)			
Cl(3)	654 (11)	838 (9)	$\frac{1}{2}$	1·7 (0·3)			
Cl(4)	1393 (10)	2830 (8)	$\frac{1}{2}$	1·0 (0·3)			
Cl(5)	3286 (13)	4033 (10)	$\frac{1}{2}$	2·6 (0·4)			
Cl(6)	4287 (12)	1146 (10)	$\frac{1}{2}$	2·0 (0·4)			
O(1)	2818 (29)	2333 (22)	0	1·5 (0·9)			
O(2)	2285 (31)	544 (25)	0	2·2 (1·0)			
O(3)	2330 (29)	1491 (22)	$\frac{1}{2}$	1·5 (0·9)			

Discussion of structure

The structure consists (Fig. 1) of an infinite polymeric chain extending along the short *c* axis, and cross-linked in the *ab* plane to symmetry-related chains by chlorine atoms [Cl(2) and Cl(5)]. The repeating element within the chain (and in fact the asymmetric unit of structure) is the twelve-atom aggregate, $Pa_3O_3Cl_6$. Each of these Pa atoms exhibits a different coordination number: 8 for Pa(1), 9 for Pa(2) and 7 for Pa(3). The complexity is further heightened by the diverse structural roles displayed by the light atoms. Oxygen atoms are three- and four-coordinate. Most of the chlorine atoms are two-coordinate of the usual bridging type; some, however, are coordinated to a third Pa atom.

At the core of this infinite chain is the Pa–O framework illustrated in Fig. 2. The O(3) atom is surrounded by four Pa atoms at the corners of a somewhat irregular tetrahedron (Pa–O(3)–Pa angles range from 104° to 120°). The O(1) and O(2) atoms are each bonded* to 3 Pa atoms. The disposition of these bonds is more nearly coplanar, sums of the angles around O(1) and O(2) being 358·2° (=2×112·9+132·4) and 353·7° (=2×112·6+128·5), respectively. This Pa–O framework bears a striking resemblance to a portion of the PaO_2 (CaF_2-type) structure (Fig. 3). (For the full PaO_2 structure there are these important differences: the Pa/O ratio is of course 1:2, and *each* O is coordinated to four Pa atoms at the corners of a *regular* tetrahedron.) In $PaOCl_2$, the Pa–O bond distances involving four-coordinate O(3) are 2·34 (three times) and 2·38 Å (σ's = 0·02–0·04 Å), slightly less, but not significantly so, than the corresponding distance of 2·39 Å in PaO_2 (from data cited by Pearson, 1958). Pa–O distances involving O(1) and O(2), 2·19, 2·23, 2·26 and 2·27 Å, are smaller in just about the proportion expected (Pauling, 1960) for a change in coordination number from 4 to 3.

Positions of the Cl atoms within the chain are illustrated in Fig. 4. Half of these Cl atoms also occupy positions which resemble those of O atoms in PaO_2. These are: Cl(1), which bridges two Pa(3) atoms; Cl(2), which bridges two Pa(1) atoms; and Cl(6), which bridges Pa(1) and Pa(3). The Cl(3) and Cl(4) atoms connect Pa(2) atoms along the chain direction, but in a different way from that in PaO_2. Whereas in PaO_2, the Pa atoms are surrounded by a cube of O atoms, in $PaOCl_2$ the 'square' of 2 Cl(3) and 2 Cl(4) atoms is rotated by about 45° relative to the 'square' of four O atoms. This arrangement of O and Cl is quite similar to that in PbFCl, a common structure-type for actinide and lanthanide oxymonochlorides (Wyckoff, 1963).

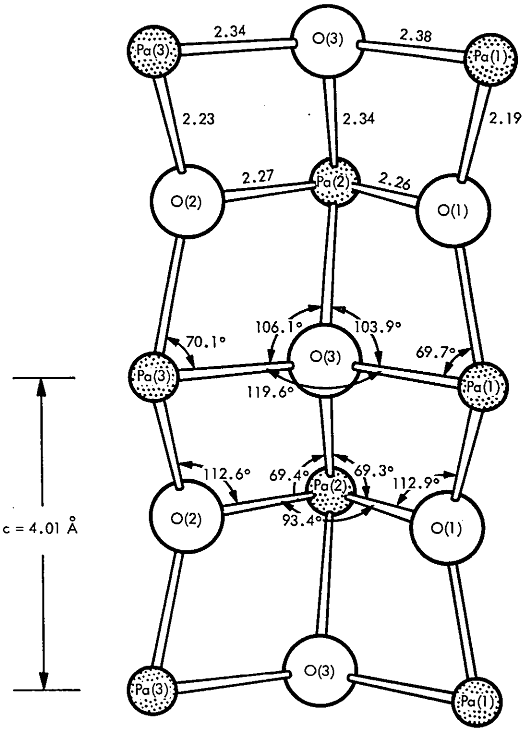

Fig. 2. Portion of Pa–O framework in $PaOCl_2$. Direction of view is approximately normal to *c* axis (the chain direction). Values of *z* increase from bottom to top of page. Values of *y* increase to right, but *y* axis is tipped ~20° into page.

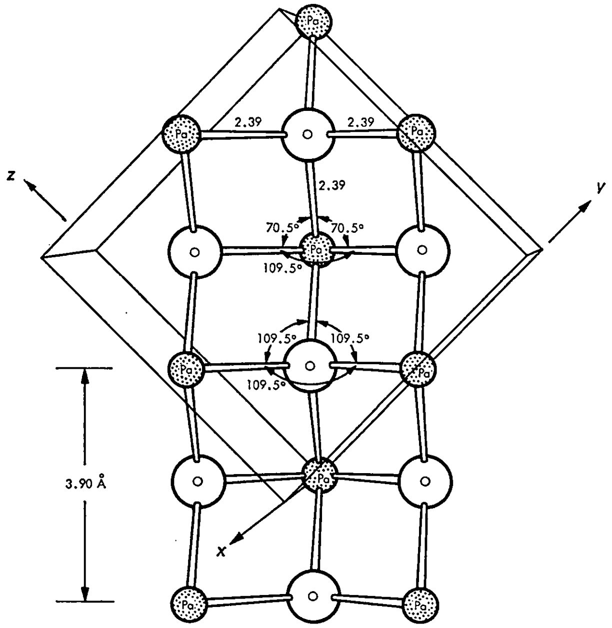

Fig. 3. Portion of the cubic PaO_2 (CaF_2-type) structure drawn to bring out resemblance to Pa–O framework in $PaOCl_2$ (Fig. 2).

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* In response to referee comment, we use the terms *coordinated* and *bonded* interchangeably in the sense that if one atom is *coordinated* to another, this carries the implication of an interaction between the two which we call a *bond.* No implication is intended that this necessarily is a two-electron, covalent bond. The interaction may even be largely electrostatic in character.

Addition of Cl(2′) from a neighboring chain completes a ninefold coordination about Pa(2) (5 Cl and 4 O atoms).

We have previously referred to the coordination number of Pa(1) as being 8, and that of Pa(3) as being 7. Actually, this distinction is not clear-cut. Fig. 4 shows a rather similar and almost mirror-imaged disposition of ligands around Pa(1) and Pa(3), an exception to this being the much closer approach of Cl(4) to Pa(1) than Cl(3) to Pa(3). The distances of interest are (Table 3): 3·08 and 3·46 Å, respectively. This skewness, rather than having both Cl(3) and Cl(4) equidistant from a Pa atom at the mean separation of 3·27 Å, is probably related to the fact that Pa(1), being bonded to two three-coordinated Cl(2) atoms, is still able to interact electronically with another Cl atom, whereas Pa(3) perhaps is saturated.

Pa–Cl distances involving the three-coordinate Cl atoms, Cl(2) and Cl(4), are somewhat longer than those involving two-coordinate Cl atoms of the simple bridging type. The Pa–Cl(2) distances are 2·93 (twice) and 2·98 Å; the Pa–Cl(4) distances are 2·91 (twice) and 3·08 Å (Table 3). Corresponding distances for bridging Cl's range from 2·74 to 2·84 Å (σ's for the Pa–Cl distances = 0·01–0·02 Å). It might also be expected that bond distances involving nine-coordinate Pa(2) would be longer than those (of a similar kind) for eight-coordinate Pa(1); greater in turn than those for seven-

Table 3. *Bond distances and selected angles*

Numbering scheme follows that of Fig. 4. Prime markings denote atoms in symmetry-related chains.

Pa(1)–2O(1)	2·191 ± 0·017 Å	Pa(2)– Cl(2′)	2·982 ± 0·018 Å
O(3)	2·376 ± 0·042	2Cl(3)	2·843 ± 0·012
2Cl(2)	2·925 ± 0·013	2Cl(4)	2·913 ± 0·011
Cl(4)	3·082 ± 0·016	Pa(3) –2O(2)	2·226 ± 0·020
Cl(5)	2·778 ± 0·019	O(3)	2·341 ± 0·040
Cl(6)	2·762 ± 0·018	2Cl(1)	2·826 ± 0·018
Pa(2)–O(1)	2·261 ± 0·043	Cl(5)	2·743 ± 0·019
O(2)	2·268 ± 0·045	Cl(6)	2·760 ± 0·018
2O(3)	2·337 ± 0·022	[Pa(3) –Cl(3)	3·462 ± 0·017]
O(1) –Pa(1)–O(1)	132·4 ± 2·1°	Pa(1) –O(1) –Pa(2)	112·9 ± 1·0°
O(1) –Pa(1)–O(3)	69·7 ± 1·0	Pa(3) –O(2) –Pa(3)	128·5 ± 2·1
Cl(2)–Pa(1)–Cl(2)	86·5 ± 0·5	Pa(2) –O(2) –Pa(3)	112·6 ± 1·1
Cl(5)–Pa(1)–Cl(6)	152·3 ± 0·6	Pa(1) –O(3) –Pa(2)	103·9 ± 1·1
O(1) –Pa(2)–O(2)	93·4 ± 1·6	Pa(1) –O(3) –Pa(3)	119·6 ± 1·8
O(1) –Pa(2)–Cl(2)	129·3 ± 1·1	Pa(2) –O(3) –Pa(3)	106·1 ± 1·1
O(2) –Pa(2)–Cl(2)	137·3 ± 1·2	Pa(2) –O(3) –Pa(2)	118·1 ± 1·8
O(1) –Pa(2)–O(3)	69·3 ± 1·1	Pa(3) –Cl(1)–Pa(3)	90·4 ± 0·6
O(2) –Pa(2)–O(3)	69·4 ± 1·1	Pa(1) –Cl(2)–Pa(1)	86·5 ± 0·5
O(3) –Pa(2)–O(3)	118·1 ± 1·8	Pa(2′)–Cl(2)–Pa(1)	136·7 ± 0·2
O(2) –Pa(3)–O(2)	128·5 ± 2·1	Pa(2) –Cl(3)–Pa(2)	89·7 ± 0·5
O(2) –Pa(3)–O(3)	70·1 ± 1·3	Pa(2) –Cl(4)–Pa(2)	87·0 ± 0·4
Cl(1)–Pa(3)–Cl(1)	90·4 ± 0·6	Pa(1) –Cl(4)–Pa(2)	76·4 ± 0·3
Cl(5)–Pa(3)–Cl(6)	163·3 ± 0·6	Pa(1′)–Cl(5)–Pa(3)	145·0 ± 0·8
Pa(1)–O(1) –Pa(1)	132·4 ± 2·1	Pa(1) –Cl(6)–Pa(3)	95·2 ± 0·6

Table 4. *Inter- and intra-chain contacts in* $PaOCl_2$

N = no. of *j* neighbors at distance *d*, *d*'s in Å.

I. Cl(*i*)···Cl(*j*) distances < 4·00 Å. *j* ≥ *i*.

i	*j*	*N*	*d*	*i*	*j*	*N*	*d*	*i*	*j*	*N*	*d*
1	4	2	3·62	2	4	2	3·46	3	5	1	3·61
1	5	2	3·85	2	5	2	3·67	3	5	1	3·62
1	6	2	3·62	2	6	2	3·66	4	5	1	3·60
1	6	2	3·74	3	3	1	3·60	4	6	1	3·70
2	3	2	3·44	3	4	1	3·73				

II. O(*i*)···Cl(*j*) distances < 3·60 Å.

i	*j*	*N*	*d*	*i*	*j*	*N*	*d*	*i*	*j*	*N*	*d*
1	2	1	3·01	2	3	2	3·24	3	4	1	2·79
1	4	2	3·09	2	5	2	3·47	3	6	1	3·05
2	1	1	2·95	3	3	1	2·81				

III. O(*i*)···O(*j*) distances ≤ 3·30 Å. *j* ≥ *i*.

i	*j*	*N*	*d*	*i*	*j*	*N*	*d*	*i*	*j*	*N*	*d*
1	2	1	3·30	1	3	2	2·61	2	3	2	2·62

σ's: Cl···Cl, 0·02 – 0·04 Å; O···Cl, 0·04 – 0·05; O···O, 0·04 Å.

coordinate Pa(3). The maximum shortening, that which accompanies a change in coordination number from nine to seven, would be about 3–4% (Pauling, 1960). There is some indication of such a trend in our results; however, at the present level of accuracy we hesitate to say this correlation is firmly established.

There is little in the literature for comparison with the present results. Using the unit-cell data for $PaCl_4$ (Zachariasen, 1954) and the atomic coordinates in isostructural UCl_4 (Mooney, 1949), one obtains Pa–Cl distances of 2·43 and 3·09 Å for Pa in eight-coordination. In $PaCl_5$ (Dodge, Smith, Johnson & Elson, 1967), Pa–Cl distances of 2·70 and 2·76 Å are found for two-coordinated Cl and seven-coordinated Pa.

Pa–Cl–Pa bond angles within the structure exhibit values ranging from 76·4° to 145·0°. The smallest angle, Pa(1)–Cl(4)–Pa(2), involves a three-coordinate Cl; the largest angle involves the chain-crosslinking Cl(5) atom. The majority of values occur near 90°. Examples include: 90·4° at Cl(1), 86·5° at Cl(2), 89·7° at Cl(3), 87·0° at Cl(4) and 95·2° at Cl(6). It is to be noted that the two three-coordinate Cl atoms differ radically in the arrangements of bonds to their three Pa neighbors. Bonds emanating from Cl(2) are essentially coplanar, the sum of the bond angles around Cl(2) being $2\times136{\cdot}7°+86{\cdot}5°=359{\cdot}9°$. Those from Cl(4) are decidedly nonplanar. The individual angles are 76·4° (twice) and 87·0°.

Coordination polyhedra for the three independent Pa atoms are shown in Fig. 5. Each polyhedron has a mirror plane as its sole element of crystallographic symmetry; each contains both oxygen and chlorine atoms as ligands. Owing to bond-length differences of some 20% between Pa–O and Pa–Cl, the following similarities with more symmetric configurations for chemically identical ligands are necessarily qualitative. In this context, we can regard the grouping around Pa(2) as resembling a trigonal prism + 3 configuration, having 4 Cl and 2 O atoms as 'prismatic' ligands and 1 Cl and 2 O atoms as 'equatorial' ligands. As some indication of the distortions, the bond angle, O(1)–Pa(2)–O(2), in the equatorial plane is pinched down from 120° to 93·4°, the angles, Cl(2)–Pa(2)–O(1) and Cl(2)–Pa(2)–O(2) are opened up to 129·3° and 137·3°, respectively. While the trigonal + 3 arrangement is the usual prototype for nine-coordination, the geometry could also be regarded as an antiprism + 1 grouping, *i.e.* 4 O, 4 Cl atoms + 1 additional Cl. The configuration around Pa(1) is perhaps easiest to categorize. This arrangement appears to be a dodecahedron of the $Mo(CN)_8^{4-}$ type (Hoard & Silverton, 1963), but with three short bonds (Pa–O) and five long bonds (Pa–Cl). Pertinent bond angles are:

Type I, O(3)–Pa(1)–Cl(4) = 69·3°,
Cl(2)–Pa(1)–Cl(2) = 86·5°;

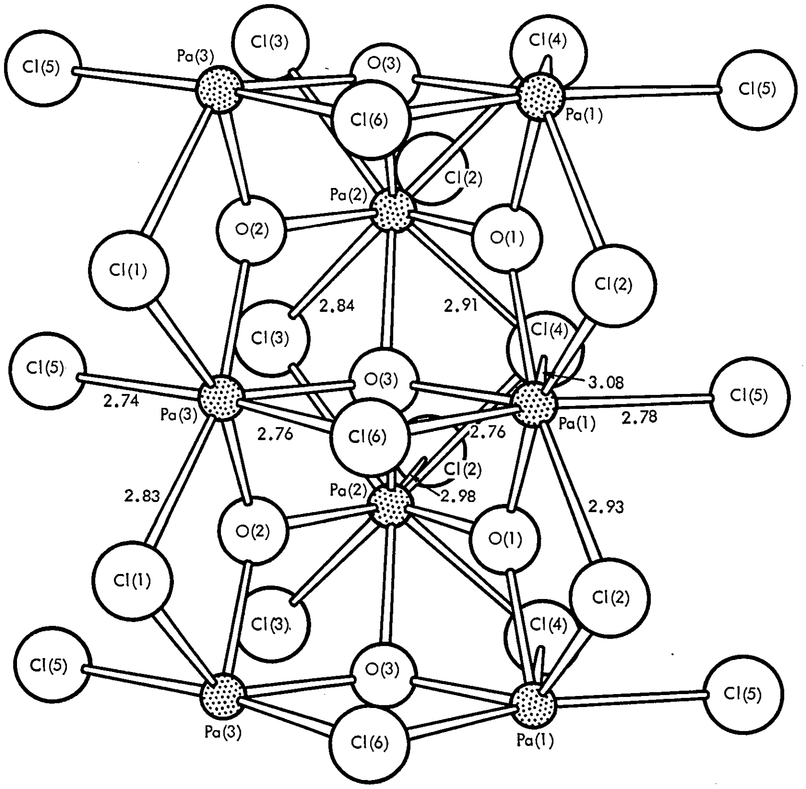

Fig. 4. Full configuration of atoms in polymeric chain in $PaOCl_2$. Direction of view is the same as in Fig. 2. All atoms are in horizontal mirror planes passing approximately out of plane of paper.

Type II, O(1)–Pa(1)–O(1) = 132·4°,
Cl(5)–Pa(1)–Cl(6) = 152·3°.

Corresponding angles for the idealized dodecahedral configuration, *i.e.* identical ligands, hard-sphere model are (Hoard & Silverton, 1963): Type I, 73·8°; Type II, 139·0°. The coordination around Pa(3) can also be considered as derived from a dodecahedron with one vertex unoccupied (or at least with one ligand well beyond normal bond distances). Bond angles analogous to those given above are: Cl(1)–Pa(3)–Cl(1) = 90·4° and O(2)–Pa(1)–O(2) = 128·7°, Cl(5)–Pa(3)–Cl(6) = 163·3°. A comparison with the previous values indicates a partial collapse to an octahedron + 1 arrangement.

Packing relations are most readily seen from Fig. 1. The infinite chains are themselves arranged in a quasi-hexagonal array when viewed along the chain direction. In addition to connections provided by bridging chlorine atoms, the chains abut against one another to give regions of local closest-packing. The inter-chain contacts are exclusively between chlorine atoms, oxygens being effectively buried within the interior of the chains. Some of the non-bonded distances are indicated in Fig. 1; a more complete list is given in Table 4.

Finally, in view of the differences between the three kinds of Pa atoms, it is not entirely clear that these atoms need have one and the same oxidation state. For example, formulations such as $(\mathrm{Pa^{IV}}_3\mathrm{O_3Cl_6})_n$ or $(\mathrm{Pa^{III}Pa^{IV}Pa^{V}O_3Cl_6})_n$ both meet the requirements of overall electrical neutrality. However, the existence of any Pa^{III} compounds is at present very uncertain (the only contender appears to be $\mathrm{PaH_3}$); hence the formulation in terms of mixed oxidation states is rendered unlikely. The same principle applies to those compositions which hypothesize one or more of the oxygen atoms as $\mathrm{OH^-}$ or $\mathrm{H_2O}$, since again Pa as Pa^{III} would be required.

We are indebted to Drs H. L. Ammon, C. K. Johnson, J. M. Stewart and A. Zalkin for furnishing copies of the several IBM-7094 programs used in the calculations. We acknowledge also with gratitude the aid of Mr D. H. Wood in the dry-box manipulations of the $\mathrm{PaOCl_2}$ samples.

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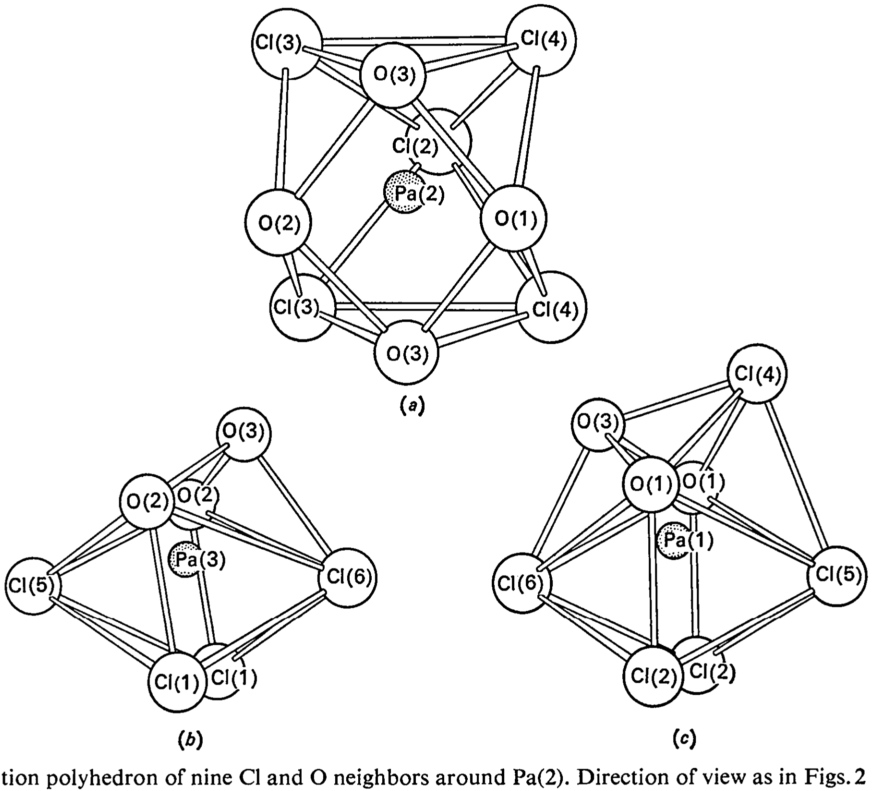

Fig. 5. (*a*) Coordination polyhedron of nine Cl and O neighbors around Pa(2). Direction of view as in Figs. 2 and 4. (*b*) Coordination polyhedron of seven Cl and O neighbors around Pa(3). A mirror plane normal to *z* axis passes through O(3), Cl(6), Cl(5) and Pa(3). (*c*) Coordination polyhedron of eight Cl and O neighbors around Pa(1). A mirror plane normal to *z* axis passes through O(3), Cl(4), Cl(5), Cl(6) and Pa(1).