Table V

Possible Hydrogen Bond Distances in α-ZrP (Ångström Units)

O_{12}–O_7	3.06 (6)
O_{10}''	2.78 (3)
O_7'	2.82 (6)
O_{10}''–O_{10}	3.07 (6)
O_{10}'	3.07 (6)[a]

[a] Next shortest distance is O_{10}–O_7 which is 3.24 (3) Å.

bonds in projection is shown in Figure 5. All three of these hydrogen bonds are intralayer bonds. The remaining hydrogen bonds form very weak interlayer bonds of the type P_3–O_{10}–H---O_{10}'' and P_3–O_{10}''–H---O_{10}'. These hydrogen bonds form a zigzag array running parallel to the *b* axis. All of the interlayer hydrogen bonds involve P_3-type phosphate groups whereas the P_2 type are all involved in intralayer hydrogen bonding.

An alternative hydrogen-bonding scheme involves the assumption that the shortest hydrogen bonds originate from the two P–OH groups with water as the acceptor atom for both these bonds. Thus, the bonding scheme would be P_2–O_7–H---O_{12} and P_3–O_{10}''–H---O_{12}. One hydrogen atom of the water forms a very long bond to O_7 and the other hydrogen forms no hydrogen bond in this scheme. There are no interlayer hydrogen bonds so that the layers are held together by van der Waals forces.

Both hydrogen-bonding schemes are speculative at present and the correct choice must await a neutron diffraction study. However, in either case the forces between layers are quite weak and one might expect cleavage parallel to the layers (001). This is in fact observed.

The zeolitic nature of the crystals and the weak forces between layers provide a basis for explaining their sieving behavior and the ready expansion of the lattice during exchange.[3] These aspects of the exchange mechanism will be discussed in a forthcoming paper.

Acknowledgment.—The authors wish to express their sincere thanks to Dr. Crispin C. Calvo of McMaster University, Hamilton, Ont., Canada, for many helpful discussions.

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The Crystal Structure of Rhenium(VII) Oxide

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Received September 23, 1968

The crystal structure of rhenium(VII) oxide, Re_2O_7, has been determined from three-dimensional single-crystal X-ray data collected by film techniques. The least-squares refinement converges to a conventional *R* factor of 0.053 for 1126 nonzero reflections. The compound crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 12.508$, $b = 15.196$, $c = 5.448$ Å, and $V = 1035.5$ Å^3. The unit cell contains 8 formula units. Measured and calculated densities are 6.14 and 6.214 g/cm^3, respectively. The structure consists of strongly distorted ReO_6 octahedra and fairly regular ReO_4 tetrahedra which are connected through corners to form polymeric double layers in the *ac* plane. The double layers have only van der Waals contacts to neighboring ones. Parallel zigzag chains of octahedra, every other chain being part of the upper or lower half of the double layer, are linked through corners of the tetrahedra in such a way that rings (o–t–o–t) (o, octahedron, t, tetrahedron) within the layers are formed. The octahedra contain three short (1.65–1.75 Å) and three long (2.06–2.16 Å) Re–O bonds, while in the tetrahedra the bond distances range from 1.68 to 1.80 Å. The structure is one of the relatively few known examples where metal atoms of the same oxidation number occur with coordination numbers 4 and 6 in the same structure. From the crystal structure the mechanisms of evaporation (to form $O_3ReOReO_3$ molecules) and of hydrolysis (where $Re_2O_7(OH_2)_2$ is formed) can be derived. In its structural and bond properties, rhenium(VII) oxide represents an intermediate between the polymeric oxides MoO_3 and WO_3 and the more covalently bonded OsO_4, which forms a molecular structure.

Introduction

The very simple crystal structure of rhenium(VI) oxide[1] has been known for a long time and has become the model for a basic structure type. Structure and bonding of solid rhenium(VII) oxide, on the other hand, have been completely unknown up to now and have been the object of speculation and controversy. A mass spectroscopic investigation[2] and vapor density measurements[3] have shown that the oxide in the gas phase consists of Re_2O_7 molecules which have to be formulated as O_3Re–O–ReO_3 with tetrahedrally coordinated rhenium. From the physical and spectroscopic properties of the compound there were

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(3) J. Noddack and W. Noddack, *Z. Anorg. Allgem. Chem.*, **181**, 1 (1929).

indications that the solid oxide does not have a simple molecular structure,[2] which could be compared with the structure of solid osmium(VIII) oxide.[4] The same properties, however, showed characteristic differences from the somewhat more heteropolar bonded d^0 oxides of molybdenum (MoO_3[5]) and tungsten (WO_3[6]).

In the course of our investigations on structural, coordination, and bond properties of transition metal–oxygen compounds we therefore studied the crystal structure of rhenium(VII) oxide in detail by X-ray diffraction (see also ref 7). The only previously known data on the structure were the cell dimensions and the probable space group which we reported some time ago,[8] essentially in accordance with approximate data given by Wilhelmi.[9]

Measurement and Reduction of the X-Ray Data

Suitable transparent crystals of dirhenium heptoxide were prepared by oxidation of rhenium powder in a stream of oxygen at 500°[3,10] and subsequent slow sublimation at normal pressure. All operations had to be done with great care to exclude moisture because of the high sensitivity of the oxide to hydrolysis.

The most frequently observed crystal forms are very thin plates (plane of the plate: (010)) and more compact prisms with the dominating planes (100), (010), and (001).

Re_2O_7 forms an orthorhombic unit cell with the refined cell dimensions $a = 12.508 \pm 0.008$, $b = 15.196 \pm 0.010$, $c = 5.448 \pm 0.005$ Å, and $V = 1035.5$ Å^3, with $Z = 8$ formula units, $D_x = 6.214$ g/cm^3, and D_m (pycnometrically) $= 6.14 \pm 0.02$ g/cm^3. All values refer to room temperature. The cell dimensions were obtained from a least-squares refinement of 16 Weissenberg reflections (NaCl calibrated, λ(Cu Kα_1) 1.54050 Å). Errors indicated are 2σ. Systematic absences were observed for reflections $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd. This leads unambiguously to the noncentrosymmetric space group $P2_12_12_1$, in which all atoms occupy the general positions 4(a): $x, y, z;\ {}^1/_2 - x, \bar{y}, {}^1/_2 + z;\ {}^1/_2 + x, {}^1/_2 - y, \bar{z};\ \bar{x}, {}^1/_2 + y, {}^1/_2 - z$. The result of the structure determination proved this space group to be correct. Owing to the extreme sensitivity of Re_2O_7 to moisture, the piezoelectric effect could not yet be measured.

The reflection data for determining the structure were recorded on integrated equiinclination Weissenberg photographs, using the multiple-film technique (Ni-filtered Cu radiation). The intensities were measured with a microdensitometer. A total of 1218 nonequivalent reflections, 92 of them with zero intensity, was obtained from two prism-shaped crystals, sealed into Lindemann capillaries, with the dimensions 0.031 × 0.022 × 0.104 mm (rotation axis c, data collected for $hk0$–$hk4$) and 0.080 × 0.023 × 0.030 mm (rotation axis a, $0kl$–$9kl$). The collected data represent 98% of the sphere with $(\sin\theta)/\lambda < 0.62$ Å^{-1}. Because of the very high linear absorption coefficient for copper Kα radiation ($\mu = 872$ cm^{-1}; $\mu R \approx 2$–3), the absorption correction was applied with special care, using accurately measured dimensions for the six crystal faces. The program written by Burnham[11] was employed for this correction. No correction for extinction was applied. After scaling the layers following the method of Hamilton, Rollett, and Sparks,[12] the data were reduced to structure factors in the usual way and brought to an approximate absolute scale according to Wilson's method.[13]

TABLE I

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR Re_2O_7[a]

	x	y	z	B, Å^2
Re(1)	0.47488 (9)	0.36970 (9)	0.5656 (3)	1.26 (2)[b]
Re(2)	0.26741 (9)	0.36367 (10)	0.0629 (3)	1.18 (2)[b]
Re(3)	0.52621 (10)	0.14267 (9)	0.3255 (3)	1.46 (3)[b]
Re(4)	0.21967 (10)	0.13646 (10)	0.8080 (3)	1.52 (3)[b]
O(1)	0.3753 (17)	0.3372 (17)	0.255 (5)	2.5 (4)
O(2)	0.5837 (17)	0.3687 (17)	0.283 (4)	2.1 (4)
O(3)	0.5006 (19)	0.2349 (14)	0.513 (4)	2.0 (4)
O(4)	0.5809 (21)	0.3822 (18)	0.766 (5)	3.2 (5)
O(5)	0.4482 (21)	0.4747 (17)	0.519 (5)	2.9 (5)
O(6)	0.4853 (24)	0.0496 (22)	0.463 (7)	4.8 (7)
O(7)	0.4480 (24)	0.1579 (22)	0.079 (7)	4.7 (7)
O(8)	0.3739 (17)	0.3375 (17)	0.762 (5)	2.4 (4)
O(9)	0.6614 (18)	0.1378 (18)	0.231 (4)	2.4 (4)
O(10)	0.2478 (21)	0.2275 (17)	0.011 (5)	2.7 (5)
O(11)	0.1606 (18)	0.3641 (18)	0.250 (5)	2.4 (4)
O(12)	0.2843 (18)	0.4727 (16)	0.017 (4)	2.4 (4)
O(13)	0.2628 (25)	0.0437 (22)	0.967 (7)	4.9 (7)
O(14)	0.2904 (18)	0.1500 (17)	0.542 (5)	2.8 (5)

[a] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits. [b] Values for the rhenium atoms before the start of refinement with anisotropic temperature factors.

Determination and Refinement of the Structure

Approximate parameters for the rhenium atoms could be derived from the direct interpretation of the three-dimensional Patterson synthesis, although some difficulties arose from the relatively large unit cell and the pseudosymmetries present in the structure.

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(12) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, **18**, 129 (1965).

(13) The calculations for this structure determination were done on an IBM 7040 (Göttingen) and on an IBM 7090 computer (Darmstadt). Besides our own programs, modified versions of programs from the Brookhaven National Laboratory system were used, among them the BNL versions of the FORDAPER Fourier program written by A. Zalkin, the Busing–Martin–Levy full-matrix least-squares program ORFLS, and the Busing–Martin–Levy ORFFE program.

TABLE II

ANISOTROPIC THERMAL PARAMETERS,[a] ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION, AND DIRECTION COSINES OF THE PRINCIPAL AXES RELATIVE TO THE CRYSTALLOGRAPHIC AXES

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	0.00209 (7)	0.00150 (5)	0.0090 (4)	0.00017 (6)	0.00001 (19)	−0.00019 (17)
Re(2)	0.00188 (7)	0.00133 (5)	0.0092 (4)	−0.00001 (6)	0.00014 (17)	−0.00032 (17)
Re(3)	0.00218 (8)	0.00151 (5)	0.0134 (5)	0.00006 (6)	0.00109 (18)	−0.00014 (18)
Re(4)	0.00243 (8)	0.00153 (5)	0.0142 (5)	0.00001 (6)	−0.00081 (19)	−0.00008 (19)

	Axis	Rms amplitude, Å	Direction cosines		
Re(1)	1	0.137 (3)	0.577	0.807	−0.124
	2	0.124 (3)	0.806	−0.538	0.249
	3	0.115 (3)	0.134	−0.244	−0.960
Re(2)	1	0.128 (3)	−0.565	0.031	−0.825
	2	0.122 (3)	−0.219	−0.969	0.114
	3	0.114 (3)	−0.796	0.245	0.554
Re(3)	1	0.151 (3)	−0.207	0.849	−0.486
	2	0.134 (2)	−0.961	−0.270	−0.063
	3	0.120 (3)	−0.185	0.454	0.871
Re(4)	1	0.153 (3)	−0.572	−0.055	0.818
	2	0.134 (2)	−0.148	0.988	−0.038
	3	0.131 (3)	−0.807	−0.143	−0.573

[a] The anisotropic temperature factors listed are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

After some cycles of least-squares refinement with the Re atoms alone, using individual isotropic temperature factors, first excluding data with $(\sin \theta)/\lambda > 0.40$ Å^{-1} and afterward including all data, the conventional R factor $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ sank to 0.11. A difference Fourier synthesis, subsequently calculated, showed a number of maxima, eight of which could be assigned unambiguously to oxygen atoms. Approximate parameters for the remaining six oxygen atoms could be taken from a second $F_o - F_c$ synthesis which included the information from the first after two further cycles of refinement. The subsequent least-squares refinement including all atoms and with individual weight factors converged after several more cycles to an R_1 value of 0.057 (without zero-intensity reflections: 0.053) and to a weighted R factor $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.059. At first isotropic temperature factors for all atoms and six scale factors were refined; later the anisotropic vibration of the Re atoms was included (constant scale factors). In this anisotropic part of the refinement the R factor dropped from 7.6% (R_1) and 7.5% (R_2) to the final values. The shifts of all 92 positional and thermal parameters were below 0.05σ in the last cycle. The expression minimized was $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors for O were taken as given from Ibers in ref 14; for Re the values calculated by Cromer and Waber[15a] were used. Anomalous dispersion corrections were applied in the case of the Re atoms (see below). The values of $\Delta f' = -5.58$ and $\Delta f'' = 5.37$ e for Cu Kα radiation have been taken from Cromer.[15b] The weighting scheme, which proved to be reasonable from an analysis of the relative errors, was: $w = (200/F_o)^2$ for $F_o > 200$, $w = 1$ for $75 \leq F_o \leq 200$, and $w = (F_o/75)$ for $F_o < 75$. The final standard deviation of an observation of unit weight is 4.2 e.

A final $F_o - F_c$ difference Fourier synthesis did not show any significant peaks higher than 1.5–2.0 e Å^{-3}, that is, 15–20% of the electron density of one oxygen atom in this structure. The final parameters after the refinement, including the standard deviations obtained from the inverse matrix, are summarized in Table I. Table II gives the anisotropic temperature factor coefficients of the Re atoms together with the dimensions and orientations of the vibration ellipsoids. It can be assumed that the vibration parameters of the Re atoms have some physical significance in spite of the refinement being only partially anisotropic, considering the fact that scattering by these atoms dominates by far and that correction for the large absorption effect has been made. The observed structure factors are compared with the final calculated ones in Table III.

In order to apply the anomalous dispersion correction properly, the absolute configuration of the structure was determined according to the Bijvoet method[16] in the course of the final refinement. After an approximate correction $f = [(f_0 + \Delta f')^2 + (\Delta f'')^2]^{1/2}$ had been applied initially during the refinement, a complete set of structure factors was calculated for both possible configurations, using the exact correction $f = f_0 + \Delta f' + i\Delta f''$.[17] Although for most of the structure factors the Bijvoet differences were negligible, a number of them were predicted to show easily measurable

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TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS) FOR DIRHENIUM HEPTOXIDE

-H	K	FCB	FCA
**** L = 0 ****			
2	0	0	3
4	0	760	796
6	0	40	32
8	0	246	238
10	0	37	42
12	0	119	119
14	0	36	33
1	1	76	79
2	1	25	30
3	1	133	140
4	1	21	38
5	1	168	182
6	1	92	97
7	1	190	181
8	1	0	9
9	1	289	295
10	1	28	31
11	1	101	96
12	1	29	26
13	1	169	174
14	1	31	26
15	1	28	23
0	2	152	163
1	2	107	97
2	2	0	1
3	2	187	196
4	2	86	78
5	2	202	197
6	2	0	11
7	2	326	316
8	2	59	57
9	2	302	316
10	2	0	8
11	2	222	222
12	2	0	8
13	2	174	170
14	2	0	8
15	2	106	100
1	3	89	79
2	3	27	33
3	3	165	169
4	3	46	46
5	3	205	199
6	3	36	33
7	3	195	191
8	3	45	44
9	3	371	390
10	3	49	56
11	3	112	118
12	3	0	5
13	3	245	239
14	3	37	42
15	3	32	28
0	4	903	1008
1	4	61	53
2	4	0	8
3	4	130	122
4	4	583	555
5	4	8	7
6	4	0	13
7	4	71	72
8	4	174	169
9	4	107	96
10	4	39	32
11	4	62	57
12	4	115	112
13	4	61	58
14	4	36	36
15	4	0	11
1	5	28	20
2	5	77	67
3	5	20	18
4	5	25	27
5	5	118	122
6	5	98	101
7	5	90	95
8	5	0	5
9	5	176	177
10	5	0	8
11	5	48	44
12	5	38	36
13	5	120	119
14	5	29	25
0	6	432	444
1	6	139	123
2	6	22	21
3	6	61	69
4	6	209	210
5	6	231	227
6	6	21	13
7	6	226	228
8	6	64	61
9	6	276	269
10	6	25	26
11	6	169	172
12	6	46	75
13	6	141	145
14	6	19	17
1	7	115	110
2	7	69	60
3	7	132	132
4	7	48	53
5	7	264	258
6	7	33	39
7	7	193	189
8	7	85	89
9	7	394	376
10	7	46	54
11	7	104	104
12	7	50	50
13	7	232	235
14	7	48	52
0	8	714	701
1	8	49	52
2	8	26	16
3	8	172	167
4	8	472	464
5	8	40	43
6	8	18	18
7	8	160	156
8	8	131	133
9	8	141	139
10	8	18	20
11	8	100	99
12	8	52	65
13	8	97	98
1	9	0	8
2	9	38	43
3	9	0	9
4	9	24	33
5	9	59	48
6	9	19	29
7	9	64	49
8	9	0	2
9	9	55	40
10	9	0	15
11	9	0	17
12	9	37	35
13	9	32	33
0	10	499	514
1	10	126	126
2	10	20	22
3	10	0	13
4	10	319	325
5	10	199	195
6	10	0	7
7	10	185	181
8	10	104	107
9	10	174	168
10	10	18	23
11	10	135	141
12	10	61	66
13	10	75	85
1	11	31	39
2	11	0	13
3	11	109	111
4	11	56	61
5	11	192	196
6	11	97	106
7	11	157	166
8	11	90	96
9	11	295	277
10	11	67	82
11	11	71	81
12	11	54	63
0	12	398	378
1	12	82	79
2	12	28	28
3	12	163	162
4	12	277	282
5	12	49	54
6	12	21	22
7	12	172	174
8	12	80	78
9	12	136	139
10	12	0	12
11	12	101	109
1	13	0	4
2	13	43	48
3	13	26	38
4	13	35	40
5	13	0	15
6	13	0	13
7	13	0	14
8	13	40	28
9	13	37	36
10	13	32	20
11	13	0	9
0	14	399	395
1	14	115	126
2	14	28	40
3	14	45	55
4	14	281	285
5	14	169	149
6	14	19	19
7	14	68	60
8	14	82	87
9	14	89	100
10	14	24	25
1	15	30	35
2	15	36	30
3	15	41	50
4	15	35	53
5	15	152	147
6	15	83	36
7	15	87	94
8	15	82	91
9	15	188	193
0	16	134	143
1	16	0	17
2	16	0	9
3	16	100	101
4	16	113	114
5	16	88	91
6	16	0	5
7	16	156	152
8	16	32	39
1	17	21	21
2	17	0	15
3	17	38	28
4	17	46	48
5	17	51	60
6	17	33	23
0	18	303	300
1	18	110	113
2	18	33	44
3	18	69	71
4	18	233	226
**** L = 1 ****			
1	0	196	192
2	0	29	20
3	0	50	37
4	0	100	101
5	0	279	268
6	0	30	28
7	0	176	180
8	0	143	152
9	0	199	193
10	0	0	6
11	0	172	164
12	0	134	139
13	0	70	70
14	0	44	41
15	0	91	90
0	1	0	16
1	1	144	159
2	1	556	520
3	1	173	166
4	1	104	96
5	1	213	204
6	1	269	287
7	1	221	222
8	1	113	110
9	1	173	170
10	1	46	53
11	1	196	204
12	1	74	67
13	1	100	99
14	1	70	72
15	1	110	114
0	2	0	4
1	2	104	110
2	2	584	617
3	2	322	303
4	2	69	59
5	2	117	110
6	2	277	276
7	2	310	328
8	2	43	29
9	2	132	131
10	2	33	31
11	2	222	225
12	2	0	3
13	2	76	81
14	2	152	140
15	2	90	91
0	3	19	24
1	3	109	107
2	3	341	337
3	3	173	167
4	3	139	162
5	3	148	148
6	3	163	165
7	3	214	211
8	3	153	163
9	3	149	140
10	3	19	12
11	3	183	173
12	3	82	85
13	3	109	109
14	3	62	71
15	3	88	90
0	4	0	11
1	4	158	152
2	4	171	168
3	4	91	88
4	4	35	36
5	4	237	231
6	4	90	88
7	4	183	187
8	4	114	111
9	4	168	177
10	4	0	16
11	4	134	159
12	4	124	129
13	4	74	71
14	4	60	55
15	4	88	81
0	5	0	5
1	5	180	174
2	5	361	373
3	5	120	121
4	5	43	44
5	5	187	196
6	5	237	228
7	5	211	216
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2	6	40	41
3	6	108	123
0	7	109	108
1	7	98	112

differences. For the 16 reflections with the largest calculated differences the observed $F_{hkl} - F_{\bar{h}kl}$ values were larger than the estimated errors of the observations. With one exception they all indicated the same configuration to be present. As a check, their *hkl* and *h̄kl* intensities were carefully remeasured on the Weissenberg films. The results which are summarized in Table IV proved (for both crystals investigated) that the configuration described here is the correct one, and the final refinement was based on this. The values in Table IV refer to the final parameters.

In assessing the reliability of this determination of the absolute configuration, it should be noted that the crystals investigated have a morphological center of symmetry (dominating planes (100), (010), (001) and centric equivalents). Therefore, possible inprecise absorption corrections cannot influence the result.

Description of the Structure and Discussion

The crystal structure of dirhenium heptoxide consists of an arrangement of polymeric double layers perpendicular to the crystallographic *b* axis, related to each other by the twofold screw axes. Between the layers there are only oxygen–oxygen van der Waals contacts. This layer structure is expressed in the macroscopic shape and the cleavability parallel to the (010) face of the crystal slabs and plates.

The structure is built of equal numbers of ReO_6 octahedra and ReO_4 tetrahedra in the following way. Zigzag chains of octahedra linked through corners run along the crystallographic *c* axis, every other chain being part of the upper and lower half of the double

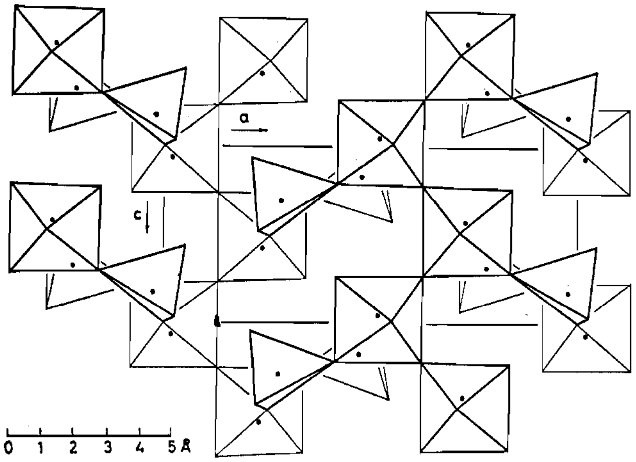

Figure 1.—Crystal structure of rhenium(VII) oxide: one of the two double layers in the unit cell, projected along the *b* axis. The layers are parallel to the *ac* plane.

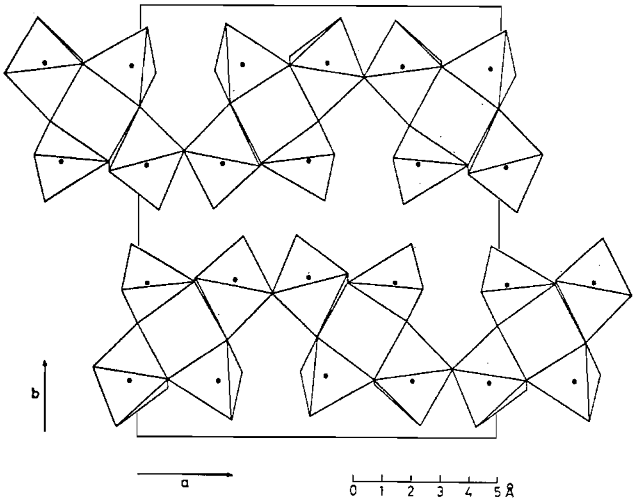

Figure 2.—Projection of the structure along the short *c* axis. The zigzag chains of ReO_6 octahedra and the layers are perpendicular to the plane of paper.

TABLE IV

DETERMINATION OF THE ABSOLUTE CONFIGURATION[a]

h	k	l	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$	$I_o(hkl)/I_o(\bar{h}\bar{k}\bar{l})$
5	1	1	197.4	204.5	<1
9	1	1	165.6	170.3	<1
1	7	1	69.4	73.2	<1
1	8	1	92.6	88.4	>1
1	11	1	26.5	28.6	<1
9	1	2	142.4	135.9	>1
9	2	2	47.0	53.5	<1
12	2	2	41.0	37.7	>1
13	3	2	58.7	55.0	>1
1	4	2	83.4	78.1	>1
12	8	2	57.3	54.0	>1
3	9	2	119.5	112.7	>1
4	10	2	45.2	53.9	<1
11	10	2	58.5	62.6	<1
8	2	3	62.0	58.4	>1
3	11	3	89.3	86.3	>1

[a] The data were collected on the quadrants *hkl* and *$\bar{h}$kl*. The numbers in Table III refer to the quadrant *$\bar{h}$kl*.

layer, respectively. These chains are connected by the ReO_4 tetrahedra to form the double layers, every tetrahedron sharing one oxygen with each of two octahedra, one in the upper chain and one in the lower. Every octahedron is thus linked to two octahedra and two tetrahedra through corners.

The double layers can also be described as a system of "rings" of four polyhedra (t–o–t–o) connected through corners. The rings themselves, which are perpendicular to the plane of the layers, are linked through corners of the octahedra resulting in a polymeric arrangement. In one unit cell there are two identical double layers with different orientations due to the twofold screw axis along *b*. Figures 1 and 2 show projections of the structure parallel and perpendicular to the layers. The structural ring unit is pictured in Figure 3.

All bond distances, the distances between neighboring oxygen atoms within the polyhedra, and the shortest Re–Re separations with their standard deviations are listed in Table V. Bond angles in and between the polyhedra are given in Table VI. The values show that the tetrahedra are reasonably regular, whereas the octahedral environment is strongly distorted. The central rhenium atom is displaced from the center parallel to one of the threefold axes of the octahedron resulting in three short Re–O bond distances (1.65–1.75 Å) and three long ones (2.05–2.16 Å) in every ReO_6 octahedron and giving a "long" and a "short" Re–O bond distance in every Re(o)–O–Re(o) bridge.

The terminal Re–O bond lengths in the tetrahedra (average value 1.70 Å) are shorter than those associated with bridging oxygens (average 1.78 Å), as should be expected owing to the higher formal orders of the terminal bonds.[18–21] The bond distances are very similar to those in the perrhenate ion of $KReO_4$ (1.77 Å)[22] or in gaseous ReO_3Cl (1.702 Å)[23] (see also ref 24). Just as for these compounds, one has to assume a considerable amount of π bonding in the terminal as well as in the bridging bonds. The same is true for the three short bonds in the octahedra. Here again the

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(18) The standard deviations obtained do not allow quantitative conclusions to be drawn about slight variations in bond strengths from differences in experimental bond lengths. These differences must be greater than 0.07–0.09 Å to be significant at the 1% level. However, the over-all quality of the determination seems to be rather better than that of similar heavy-atom structures solved from film data (usual σ values 0.04–0.06 Å). Given a complex very heavy atom–light atom structure like this only very carefully collected (and multiply observed), counter data can give substantially higher accuracy. Ibers and coworkers[19,20] have also pointed this out reporting from highly accurate counter data Re–N bond distances with σ = 0.011 Å. Similarly accurate Re–O bond lengths have been reported recently.[21]

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TABLE V

PRINCIPAL INTERATOMIC DISTANCES (IN Å) WITHIN THE ReO_6 AND ReO_4 POLYHEDRA[a]

Bond distances						Mean
Re(1)–O(1)	A[b]	2.160(26)	Re(2)–O(8)	A	2.151(25)	2.16
Re(1)–O(2)	B	2.054(23)	Re(2)–O(9)	B	2.080(24)	2.08
Re(1)–O(3)	B	2.093(22)	Re(2)–O(10)	B	2.103(25)	
Re(1)–O(4)	C	1.727(28)	Re(2)–O(11)	C	1.682(25)	1.69
Re(1)–O(5)	C	1.650(26)	Re(2)–O(12)	C	1.690(24)	
Re(1)–O(8)	A	1.725(24)	Re(2)–O(1)	A	1.753(24)	1.74
Re(3)–O(3)	B	1.764(22)	Re(4)–O(2)	B	1.773(21)	1.78
Re(3)–O(9)	B	1.769(22)	Re(4)–O(10)	B	1.806(25)	
Re(3)–O(6)	D	1.680(33)	Re(4)–O(13)	D	1.742(34)	1.70
Re(3)–O(7)	D	1.677(33)	Re(4)–O(14)	D	1.709(25)	

Re(1) octahedron		Re(2) octahedron	
O(1)–O(2)	2.66(3)	O(8)–O(9)	2.69(3)
O(1)–O(3)	2.62(3)	O(8)–O(10)	2.67(3)
O(1)–O(5)	2.70(4)	O(8)–O(12)	2.72(3)
O(1)–O(8)	2.76(4)	O(1)–O(8)	2.69(4)
O(2)–O(3)	2.60(3)	O(9)–O(10)	2.67(4)
O(2)–O(4)	2.64(4)	O(9)–O(11)	2.62(3)
O(2)–O(5)	2.67(3)	O(9)–O(12)	2.65(3)
O(3)–O(4)	2.81(4)	O(10)–O(11)	2.68(4)
O(3)–O(8)	2.61(3)	O(1)–O(10)	2.66(4)
O(4)–O(8)	2.68(3)	O(1)–O(11)	2.72(4)
O(4)–O(5)	2.56(4)	O(11)–O(12)	2.60(3)
O(5)–O(8)	2.64(4)	O(1)–O(12)	2.69(3)
Mean	2.66	Mean	2.67

Re(3) tetrahedron		Re(4) tetrahedron	
O(3)–O(6)	2.84(4)	O(2)–O(13)	2.94(4)
O(3)–O(7)	2.72(4)	O(2)–O(14)	2.77(3)
O(3)–O(9)	2.93(3)	O(2)–O(10)	2.99(3)
O(6)–O(7)	2.71(5)	O(13)–O(14)	2.84(5)
O(6)–O(9)	2.88(4)	O(10)–O(13)	2.81(4)
O(7)–O(9)	2.81(4)	O(10)–O(14)	2.86(4)
Mean	2.82	Mean	2.87

Rhenium–rhenium separations between linked polyhedra			
Re(1)–Re(2)	3.753(3)	Re(1)–Re(4)	3.678(3)
Re(1)–Re(2)	3.774(3)	Re(2)–Re(3)	3.686(3)
Re(1)–Re(3)	3.745(3)	Re(2)–Re(4)	3.769(3)

[a] All distances in the lists for the two crystallographically independent equal polyhedra are given in the same order to facilitate easy comparison. [b] Functions of the oxygen atom: A, bridging atom, octahedron–octahedron; B, bridging atom, octahedron–tetrahedron; C, terminal atom within octahedron; D, terminal atom within tetrahedron.

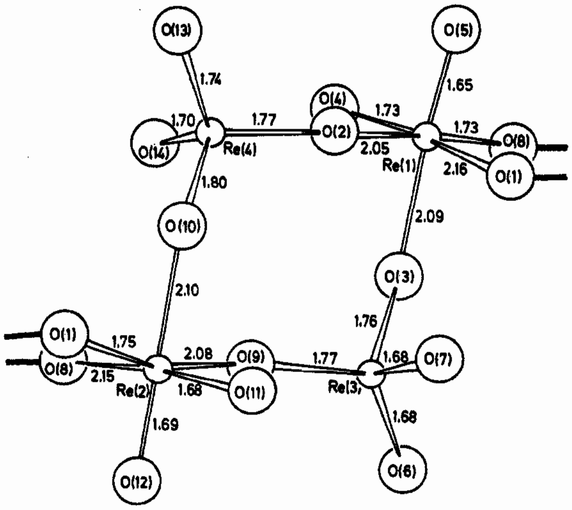

Figure 3.—Asymmetrical unit of the Re_2O_7 structure with experimentally determined bond distances in ångströms. The direction of the view is approximately along *c*.

TABLE VI

BOND ANGLES (IN DEG) IN AND BETWEEN THE ReO_n POLYHEDRA

O(1)–Re(1)–O(2)	78.1(9)	O(8)–Re(2)–O(9)	78.8(11)
O(1)–Re(1)–O(3)	76.0(9)	O(8)–Re(2)–O(10)	77.8(10)
O(1)–Re(1)–O(4)	164.3(11)	O(8)–Re(2)–O(11)	163.0(11)
O(1)–Re(1)–O(5)	89.0(12)	O(8)–Re(2)–O(12)	89.5(11)
O(1)–Re(1)–O(8)	90.0(12)	O(1)–Re(2)–O(8)	86.3(12)
O(2)–Re(1)–O(3)	77.8(10)	O(9)–Re(2)–O(10)	79.2(11)
O(2)–Re(1)–O(4)	88.0(11)	O(9)–Re(2)–O(11)	87.7(11)
O(2)–Re(1)–O(5)	91.5(12)	O(9)–Re(2)–O(12)	88.6(12)
O(2)–Re(1)–O(8)	161.2(11)	O(1)–Re(2)–O(9)	161.3(11)
O(3)–Re(1)–O(4)	94.4(11)	O(10)–Re(2)–O(11)	89.5(12)
O(3)–Re(1)–O(5)	162.9(11)	O(10)–Re(2)–O(12)	163.9(11)
O(3)–Re(1)–O(8)	85.4(11)	O(1)–Re(2)–O(10)	86.7(11)
O(4)–Re(1)–O(5)	98.4(13)	O(11)–Re(2)–O(12)	100.7(11)
O(4)–Re(1)–O(8)	101.7(12)	O(1)–Re(2)–O(11)	104.5(11)
O(5)–Re(1)–O(8)	102.8(12)	O(1)–Re(2)–O(12)	102.5(12)
O(3)–Re(3)–O(6)	110.8(14)	O(10)–Re(4)–O(13)	104.8(14)
O(3)–Re(3)–O(7)	104.3(13)	O(10)–Re(4)–O(14)	109.1(12)
O(3)–Re(3)–O(9)	112.1(12)	O(2)–Re(4)–O(10)	113.1(12)
O(6)–Re(3)–O(7)	107.2(16)	O(13)–Re(4)–O(14)	110.9(15)
O(6)–Re(3)–O(9)	112.7(14)	O(2)–Re(4)–O(13)	113.6(13)
O(7)–Re(3)–O(9)	109.3(14)	O(2)–Re(4)–O(14)	105.4(11)
Re(1)–O(1)–Re(2)	149.2(15)	Re(1)–O(2)–Re(4)	147.7(15)
Re(1)–O(8)–Re(2)	150.9(15)	Re(2)–O(9)–Re(3)	146.6(15)
Re(1)–O(3)–Re(3)	152.4(15)	Re(2)–O(10)–Re(4)	149.0(15)

bridging bond (mean 1.74 Å) seems to be somewhat longer than the two terminal bonds (mean 1.69 Å). The strong distortion of the coordination octahedra is a common feature in complexes and oxides expecially of group IV–VII transition metals. Reasons and examples of these distortions have been discussed.[25] The kind of distortion observed in the present case has been found by Magnéli[26] and Kihlborg[27] in a similar form in the two modifications of Mo_4O_{11}. The Re_2O_7 structure has features in common with the $Mo_2O_7^{2-}$ ion in $Na_2Mo_2O_7$ which consists of polymeric chains with (like Re_2O_7) equal proportions of MO_6 octahedra and MO_4 tetrahedra connected through corners.[28] However the connection scheme and the distortion of the octahedra in the dimolybdate ion (two long, two intermediate, two short bond distances) are different.

If the partly ionic character of the long Re–O bonds >2.0 Å is stressed, the structure of rhenium(VII) oxide can be described as being close to an arrangement of ReO_4^- anions (the tetrahedra) and ReO_3^+ cations.

It is interesting to note that there is a strong pseudosymmetry in the structure. Each of the two double layers in the unit cell has additional pseudoinversion centers at approximately $^3/_8$, $^3/_4$, $^1/_4$, etc., and $^5/_8$, $^1/_4$, $^1/_4$, etc., which, taken as real, apply only to half of the structure and do not lead to a higher symmetry of the structure as a whole.

The interpretation of the observed bond distances in terms of quantitative π-bond contributions is difficult. The very complicated infrared spectrum[2,29] can only lead to approximate force constants. An estimation of the bond orders can be done on the basis of the ideas given by Cotton and Lippard[30] and Doedens and Ibers.[20] Starting from data for some octahedral Re(V) halo complexes, a theoretical Re–O single bond length of 2.04 Å and a double bond length of 1.86 Å were obtained. This extrapolates according to Pauling's empirical rule to a theoretical triple bond distance of 1.75 Å. As was pointed out, however,[20] these values, derived from systems in which nonbonded interactions of the ligands determine the mean bond distances, predict very high bond orders in less "stressed" polyhedra with lower coordination numbers. In the case of Re_2O_7 the observed bond lengths would correspond to an unreasonably high sum of Re–O bond orders in the octahedra (12.5) as well as in the tetrahedra (12.3). It seems that a Re–O bond order–bond length curve not far from the one derived for Mo–O bonds[31] is closest to reality, giving approximate bond orders of ~1 for the long octahedral bonds above 2 Å and of 1.6–3.0 for the short ones below 1.80 Å. This predicts approximate total Re–O bond orders of 10.2 in the octahedra and of 9.0 in the tetrahedra, these values being reasonable and close to the numbers to be expected from molecular orbital considerations.

The packing of the space-determining oxygens in the Re_2O_7 structure is relatively open. The O–O contact distances in the octahedra (mean values 2.66 and 2.67 Å) are not far from the possible minimum (thus causing the "rattling" effect and distortion in the concept of Orgel[25]). All other O–O contacts in the tetrahedra (mean values 2.82 and 2.87 Å) and extrapolyhedral O–O distances (>2.75 Å) are significantly longer. Every O atom in the structure is surrounded by 10–12 others within 2.56–3.5 Å. The quotient V/n_O (V, volume of the unit cell; n_O, number of oxygens in the cell), which gives a measure for the packing density, is 18.9 Å^3 for Re_2O_7. Values for other d^0 oxides are (Å^3): MoO_3, 16.9; WO_3 (monoclinic), 17.6; WO_3 (tetragonal), 18.2; OsO_4, 20.7. Like other structural features these numbers place rhenium(VII) oxide between the polymeric oxides MoO_3 and WO_3 and the more covalently bonded OsO_4, confirming its character as being a compromise between an ionic and a molecular structure.

On the basis of the crystal structure determined, it is possible to derive a plausible evaporation mechanism and to explain the relatively high volatility of rhenium(VII) oxide. Thermal cleavage of two of the long, weak Re–O bonds per octahedron, together with a slight change in hybridization at these Re atoms, is sufficient to yield the Re_2O_7 molecule with tetrahedral coordination around all Re atoms as is assumed in the gas phase (see below). The configuration of the Re_2O_7 molecule is already "pre-formed" in the structure of the polymeric solid.

In this context it may be of significance that in the process of preparing the oxide one obtains, besides the yellow crystalline Re_2O_7, a small quantity of a poorly defined white amorphous solid, which had been erroneously described to be rhenium(VIII) oxide by its first investigators.[3] It is very probable that this is a second "molecular" modification of solid Re_2O_7, formed by direct condensation (quenching) of the gas-phase molecules, without rearrangement of the bonding system.

It is interesting to compare the features of the structure with those of solid perrhenic acid which is the primary hydrolysis product of Re_2O_7 and which is also formed on evaporation of aqueous solutions. Recently we succeeded in characterizing this compound as dirhenium diaquoheptoxide $Re_2O_7(OH_2)_2$. The crystal structure shows isolated molecules which consist of one ReO_4 tetrahedron and one $ReO_4(OH_2)_2$ octahedron connected through one oxygen corner.[32]

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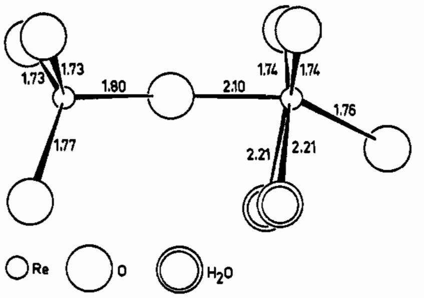

Figure 4.—Configuration and bond distances in ångströms of the primary hydrolysis product of Re_2O_7: dirhenium diaquoheptoxide, $Re_2O_7(OH_2)_2$ ("solid perrhenic acid").[32]

If the dimensions of the molecule, as given in Figure 4, are compared with the bond distances in Re_2O_7, a close resemblance is evident. Of special theoretical interest is the fact that the kind of distortion of the octahedra is analogous in both compounds.

The mechanism of the partial hydrolysis of rhenium(VII) oxide to $Re_2O_7(OH_2)_2$ can be assumed to be similar to the evaporation mechanism. The Re–O bonds which are cleaved hydrolytically are the same which are broken in the process of evaporation: Re(1)–O(1), Re(2)–O(8) plus either Re(1)–O(2), Re(2)–O(9) or Re(1)–O(3), Re(2)–O(10). If Figures 3 and 4 are compared, the structural relationships among Re_2O_7(s), Re_2O_7(g), and $Re_2O_7(OH_2)_2$ can be visualized.

Thermal Vibrations.—The temperature factor coefficients are significantly larger for the tetrahedrally coordinated Re atoms than for those in the octahedra (see Tables I and II). The shortest axes of the vibration ellipsoids for the octahedral Re atoms were found to be along the directions in which the metal atoms are displaced from the centers of the octahedra. These features are physically reasonable, and they are observed almost identically in two crystallographically independent polyhedra. In view of the esd's the parameter differences of Table II are to be regarded as possibly significant. The oxygen atoms O(6), O(7), and O(13), representing terminal atoms in the tetrahedra, show substantially (and possibly significantly) higher temperature factors than the rest.

Acknowledgments.—We wish to thank Professor Dr. O. Glemser for his generous support of our work, and we thank Dr. W. C. Hamilton and Dr. D. F. Koenig for supplying programs from the Brookhaven National Laboratory library. The assistance of Dipl.-Chem. G. Wagner in preparing the oxide is greatly appreciated.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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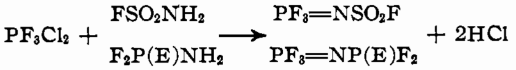
The Synthesis of Trifluorophosphazo Compounds

BY MAX LUSTIG

Received August 19, 1968

Trifluorophosphazosulfuryl fluoride, $PF_3{=}NSO_2F$, trifluorophosphazophosphoryl fluoride, $PF_3{=}NP(O)F_2$, and trifluorophosphazothiophosphoryl fluoride, $PF_3{=}NP(S)F_2$, are prepared by the reaction between phosphorus dichloride trifluoride, PF_3Cl_2, and sulfuramidic fluoride, FSO_2NH_2, phosphoramidic difluoride, $F_2P(O)NH_2$, and thiophosphoramidic difluoride, $F_2P(S)NH_2$, respectively. Some properties of these new compounds, including $F_2P(S)NH_2$, have been studied.

Trichlorophosphazophosphoryl difluoride, $PCl_3{=}NP(O)F_2$, and several of its derivatives[1] and trichlorophosphazosulfuryl fluoride, $PCl_3{=}NSO_2F$,[2] have recently been reported. However, attempts to exchange the chlorine atoms bound to the phosphorus with fluorine have been unsuccessful.[2] A method has now been found for the preparation of perfluorinated phosphazosulfuryl and -phosphoryl compounds



$$PF_3Cl_2 + \begin{matrix} FSO_2NH_2 \\ F_2P(E)NH_2 \end{matrix} \longrightarrow \begin{matrix} PF_3{=}NSO_2F \\ PF_3{=}NP(E)F_2 \end{matrix} + 2HCl$$

where E = O or S. Thiophosphoramidic difluoride, a new compound and the precursor to trifluorophosphazothiophosphoryl difluoride, is prepared by ammonolysis of μ-oxo-bis(thiophosphoryl difluoride), $F_2P(S)OP(S)F_2$, in a manner similar to the synthesis of phosphoramidic difluoride from pyrophosphoryl fluoride.

Experimental Section

Reagents.—The amidic compounds FSO_2NH_2[2] and POF_2NH_2[3] were prepared by the literature methods. Established methods were used to synthesize pyrophosphoryl fluoride[4] and μ-oxo-bis(thiophosphoryl difluoride).[5] Lecture bottles of PF_3 and Cl_2 were

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