TABLE IV

DERIVATIVES CHARACTERISTIC OF β-$ReCl_4$ AND OBTAINED WITH THE PRODUCT OF CCl_4–$ReO_2 \cdot nH_2O$ AT HIGH TEMPERATURE

	Yield, %		% compn									
			C		H		N		S		Cl	
Derivative	Found	Lit.	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$	36	39	33.6	33.7	6.4	6.6	2.5	2.7	...	...	24.9	24.4
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_9$	46	...	32.7	32.7	6.1	6.0	2.4	2.7	...	...	27.2	26.5
$[(C_6H_5)_4As]_2Re_2Cl_8$	50	46	...	...	...	...	...	...	...	...	...	...
$[(C_6H_5)_4As]_2Re_2Cl_9$	44	52	...	...	...	...	...	...	...	...	...	...
$ReCl_3(tu)_3 \cdot {}^1/_3(CH_3COCH_3)$[a]	...	...	8.9	8.2	2.6	3.4	15.5	15.3	17.8	17.8	19.7	18.8
$ReCl_3(C_6H_5)_3P$	32	50	39.0	38.9	7.7	3.4	...	...	...	...	19.2	18.3
$ReOCl_3 \cdot$ bipy[b]	...	...	25.8	26.2	1.7	2.0	6.0	6.1	...	...	22.9	22.5
$ReOCl_3[(C_6H_5)_3P]_2$	32	...	52.0	51.0	3.6	4.2	...	...	...	...	...	...
(bipyH)$ReOCl_4$	...	...	23.9	23.3	1.8	2.1	5.6	4.9	...	...	...	...
$Re_2O_3(C_5H_5N)_4Cl_4$	...	...	27.3	27.5	2.33	2.33	6.3	5.4	...	...	...	...
Green ppt from $ReCl_4^-$, C_5H_5N–C_2H_6O	...	...	18.2[4]	16.2	1.9[4]	1.9	2.9[4]	3.3	...	...	...	...

[a] tu = thiourea. [b] bipy = 2,2′-bipyridyl.

chemical properties of β-$ReCl_4$ so that these methods are now available as starting points for examining new derivatives unique to $ReCl_4$.

Experimental Section

Thionyl Chloride.—This was purified by the linseed oil–quinoline method[25] and fractionated (bp 75–76°, lit.[25] bp 77°). The origin of carbon in our α-$ReCl_4$ clearly results from contaminated thionyl chloride, possibly from the ingredients used in purifying it. However, some purification of $SOCl_2$ is essential since very poor results are obtained with crude or recovered $SOCl_2$ (*viz.*, preparations 1 and 2, Table I). Colton, *et al.*, did not state how they purified their $SOCl_2$.

Hydrated Rhenium Dioxide.—Preparations 1–13 employed dioxide from the reduction of $KReO_4$ with zinc and hydrochloric acid. Although this material contains detectable amounts of zinc (probably as metallic fragments), the over-all results were the same as in preparations 14–28 where dioxide from the hydrolysis of $ReCl_5$ was employed. The precipitated dioxide was washed with water and acetone and then vacuum dried at room temperature.

The First Transition Element Hydroxides.—The colloidal precipitates from the action of alkali on the appropriate chloride were washed (assisted by centrifugation for separation) and dried as for $ReO_2 \cdot nH_2O$.

Analyses.—Cl was determined by potentiometric titration and Re by the α-furil dioxime method.[26] The remaining transition elements were analyzed by flame spectrophotometry against standard solutions; C, H, N, and S were determined by commercial microanalyses.

Reaction Products.—These were efficiently separated from the $SOCl_2$ phase by centrifugation and decantation. The chloride products were handled under dry nitrogen and dried in vacuum.

Acknowledgment.—We are grateful to Dr. J. E. Fergusson for his unpublished results and the interesting discussion with J. C. S.

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[25] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 189.

[26] V. W. Meloche, R. L. Martin, and W. H. Webb, *Anal. Chem.*, **29**, 527 (1957).

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Crystallographic Studies on Polynuclear Rhenium Carbonyl Hydrides and Anions. II.[1] The Characterization of $[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$

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The tetra-*n*-butylammonium salt of the hexadecacarbonyltetrarhenium dianion—$[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$—crystallizes as deep red parallelepipeds in the centrosymmetric monoclinic space group C2/c (no. 15; C_{2h}^6) with $a = 24.65 \pm 0.04$ Å, $b = 12.93 \pm 0.02$ Å, $c = 19.49 \pm 0.03$ Å, $\beta = 107.7 \pm 0.2°$, $Z = 4$. Observed and calculated densities are 1.89 ± 0.01 and 1.887 g cm^{-3}, respectively. A single-crystal X-ray diffraction study has been completed. Data to $\sin \theta = 0.37$ (Mo Kα radiation) were collected with a 0.01°-incrementing Buerger automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 10.65\%$ for 2696 independent nonzero reflections. The crystal consists of discrete $Re_4(CO)_{16}^{2-}$ and $(n\text{-}C_4H_9)_4N^+$ ions. The $Re_4(CO)_{16}^{2-}$ ion has crystallographically imposed C_2 symmetry with the rhenium atom skeleton defining two fused, coplanar, approximately equilateral triangles. Individual rhenium–rhenium bond distances range from 2.956 ± 0.007 to 3.024 ± 0.007 Å. Each rhenium atom is associated with four terminal carbonyl ligands, two of which are approximately *axial* and two approximately *equatorial*. The $Re_4(CO)_{16}^{2-}$ ion distorts from idealized D_{2h} symmetry, probably as a result of intramolecular oxygen···oxygen contacts. The tetra-*n*-butylammonium ions have the expected configuration, but one of the *n*-butyl chains appears to have a disordered $-CH_2-CH_3$ moiety.

Introduction

The reaction of dirhenium decacarbonyl with sodium borohydride (in tetrahydrofuran) gives rise to a solution with an intense red coloration.[3] Evidence that this solution contains a number of different rhenium–carbonyl species comes from (i) the highly complicated infrared absorption spectrum in the carbonyl stretching

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[1] Part I: M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

[2] On leave from the Department of Chemistry, University of California at Los Angeles; supported by Grant GP-6720, from the National Science Foundation.

[3] R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 6374 (1967).

region and (ii) the results of acid hydrolysis, which yields $HRe(CO)_5$, $Re_2(CO)_{10}$, $H_3Re_3(CO)_{12}$, and $HRe_3(CO)_{14}$.[3] The addition of tetra-*n*-butylammonium iodide to the red solution gives rise to a red, crystalline salt.[4] A crystallographic analysis of this material was originally undertaken because it was believed that the compound might be the $(n\text{-}C_4H_9)_4N^+$ salt of an anionic rhenium–carbonyl–hydride precursor to $HRe_3(CO)_{14}$ (possibly $HRe_2(CO)_9^-$). However, the completed crystallographic study (*vide infra*) shows the red salt to be derived from the polynuclear rhenium carbonyl anion $Re_4(CO)_{16}^{2-}$. This structural analysis thus represents the characterization of a compound of unknown formula and stereochemistry. A preliminary account of this work has appeared previously.[3]

Unit Cell and Space Group

Crystals of the material under investigation (later found to be $[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$) were prepared by Mr. B. Fontal and supplied to us by Professor H. D. Kaesz of the University of California at Los Angeles. The complex crystallizes as dark red, air-stable crystals which do not appear to be X-ray sensitive.

Optical examination and the observed reciprocal lattice symmetry (C_{2h}; 2/m) indicated that the crystals belonged to the monoclinic system. Unit cell parameters obtained from calibrated ($a_{NaCl} = 5.640$ Å) $h0l$ and $0kl$ precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 22 ± 2° are: $a = 24.65 \pm 0.04$ Å, $b = 12.93 \pm 0.02$ Å, $c = 19.49 \pm 0.03$ Å, and $\beta = 107.7 \pm 0.2°$. The unit cell volume is 5918 Å^3.

A careful survey of $hk0$ and $hk1$ Weissenberg photographs and $h0l$, $h1l$, $0kl$, and $1kl$ precession photographs revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$, compatible with space group Cc (no. 9) or C2/c (no. 15).

The density of the compound, measured by flotation in an iodomethane–carbon tetrachloride mixture, was 1.89 ± 0.01 g cm^{-3}. This is rather lower than the value calculated for $[(n\text{-}C_4H_9)_4N][HRe_2(CO)_9]$ ($\rho = 1.99$ g cm^{-3} for $M = 866$, $Z = 8$) but was found (at a later date) to be consistent with the density calculated for $[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$ ($\rho = 1.887$ g cm^{-3} for $M = 1678$, $Z = 4$).

It should be emphasized that, at this stage of the analysis, it was not possible to determine unambiguously either the space group or the number of molecules per unit cell. The subsequent solution to the Patterson synthesis and the determination of the crystal structure (*vide infra*) showed the true space group to be the centrosymmetric C2/c (no. 15, C_{2h}^6).

Collection and Reduction of the X-Ray Diffraction Data

Two crystals were used during the process of collecting data. Crystal I (0.12 × 0.12 × 0.44 mm) was close to cylindrical in cross section and was mounted along its extended c direction. Crystal II (a platelike parallelepiped of thickness 0.16 mm, with face diagonals 0.71 and 0.20 mm) was obtained by carefully slicing a large, freshly prepared crystal and was mounted along the 0.71-mm diagonal of its largest face—*i.e.*, the b direction. Each crystal was glued to a lithium borate fiber and was inserted into a 0.2-mm diameter thin-walled capillary.

Intensity data (Mo Kα radiation; $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01°-incrementing Buerger automated diffractometer, using the standard "stationary-background, ω-scan, stationary-background" counting sequence. Equiinclination Weissenberg geometry was used throughout the analysis, The apparatus, experimental procedure, and general precautions have been described at length in a previous publication.[5] Details pertinent to this particular crystallographic analysis include: (i) The angle scanned (ω) is given by $\omega = [1.5 + (0.8/L)]°$, where $1/L$ is the Lorentz factor. (ii) The speed of the ω scan was 2°/min. (iii) Each background (B_1 and B_2) was measured for one-fourth the time of the main scan (C counts). (iv) Within each zone the stability of the system was monitored by remeasuring a carefully preselected check reflection after each batch of 20 reflections had been collected. [No appreciable—*i.e.*, $\geqslant 3(\text{count})^{1/2}$—variation from the mean was detected.]

$I(hkl)$, the integrated intensity of the reflection hkl, was calculated as: $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$. Data were assigned standard deviations according to the scheme: $I(hkl) \geqslant 625$, $\sigma(hkl) = 0.1[I(hkl)]$; $I(hkl) < 625$, $\sigma(hkl) = 2.5[I(hkl)]^{1/2}$. Reflections were omitted from the subsequent analysis if $I(hkl) \leqslant 3[2B_1(hkl) + 2B_2(hkl)]^{1/2}$.

Data for the reflections in the quadrants hkL and $\bar{h}kL$ (L = 0–20) were collected from crystal I, and data for hKl and $\bar{h}Kl$ (K = 0–13) were collected from crystal II. [In each case this represents a single set of diffraction data complete to $\sin\theta = 0.37$, save for the few reflections with $\theta \leqslant 4°$ that are shielded by the lead backstop. The limit $\sin\theta_{max} = 0.37$ is high enough to include every reflection visible on long-exposure Weissenberg or precession photographs taken with Mo Kα radiation.] All data were next corrected for Lorentz and polarization effects ($(LP)^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)$). Although the absorption coefficient (μ) is 87.12 cm^{-1} for Mo Kα radiation, crystal I is close to cylindrical in shape and no absorption corrections were applied to data from this crystal. [It may be noted that with $R = 0.006$ cm, $\mu R = 0.52$ and the variation in transmission coefficient over the range $0 \leqslant \theta \leqslant 22°$ is less than 1.5%.[6]] For crystal II a specific absorption correction was made, using a local modification of Burnham's GNABS;[7] transmission factors were found to vary between 0.19 and 0.27.

The 35 zones of data were now correlated by means of a least-squares procedure which minimized a sum of

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[4] Precise details of the isolation of this salt are contained in ref 3.

[5] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

[6] W. L. Bond in "International Tables for X-Ray Crystallography," Vol. 2, The Kynoch Press, Birmingham, England, 1959, Table 5.3.5B, p 295.

[7] C. W. Burnham, GNABS, a general absorption program for the IBM 7094.

Table I

Observed and Calculated Structure Factors (in electrons) for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_4(\text{CO})_{16}]^a$

H	L	FO	FC
K = 0			
6	0	167	154
8	0	644	746
10	0	751	856
12	0	305	267
14	0	107	40
16	0	254	253
18	0	390	399
20	0	268	240
22	0	72	25
24	0	79	20
-20	2	295	290
-18	2	423	431
-16	2	194	183
-12	2	308	346
-10	2	821	905
-8	2	573	608
-6	2	341	327
6	2	169	174
8	2	395	452
10	2	479	558
12	2	172	202
16	2	231	235
18	2	380	388
20	2	210	186
-24	4	59	21
-22	4	72	49
-20	4	341	337
-18	4	401	431
-16	4	141	133
-12	4	506	487
-10	4	712	749
-8	4	276	288
-6	4	200	190
-4	4	101	87
-2	4	556	732
0	4	762	901
2	4	136	137
4	4	45	18
6	4	227	235
8	4	508	637
10	4	439	515
12	4	87	85
16	4	221	238
18	4	302	319
20	4	147	146
22	4	44	11
-26	6	117	99
-22	6	111	108
-20	6	366	366
-18	6	374	375
-16	6	159	148
-12	6	444	456
-10	6	739	772
-8	6	357	375
-6	6	59	47
-4	6	117	118
-2	6	855	975
0	6	1000	1105
2	6	214	220
6	6	359	365
8	6	580	630
10	6	409	457
12	6	81	70
16	6	241	243
18	6	252	259
20	6	99	107
-26	8	100	77
-22	8	116	121
-20	8	362	360
-18	8	343	335
-16	8	104	79
-14	8	32	11
-12	8	384	419
-10	8	598	647
-8	8	368	395
-6	8	29	30
-4	8	237	232
-2	8	771	863
0	8	698	746
2	8	154	165
4	8	42	46
6	8	306	320
8	8	497	544
10	8	271	319
14	8	55	49
16	8	241	239
18	8	217	209
20	8	63	56
-24	10	63	27
-22	10	152	138
-20	10	384	358
-18	10	302	308
-16	10	60	48
-14	10	53	42
-12	10	424	434
-10	10	493	531
-8	10	254	275
-4	10	237	255
-2	10	632	690
0	10	513	529
2	10	102	99
6	10	290	303
8	10	411	426
10	10	244	232
12	10	44	28
14	10	72	56
16	10	224	205
18	10	170	158
-24	12	58	6
-22	12	166	172
-20	12	338	334
-18	12	236	229
-14	12	141	125
-12	12	426	446
-10	12	482	504
-8	12	192	201
-4	12	290	297
-2	12	607	621
0	12	446	446
4	12	70	42
6	12	261	269
8	12	296	314
10	12	171	148
12	12	42	11
14	12	84	60
-22	14	167	174
-20	14	295	309
-18	14	167	171
-14	14	144	110
-12	14	343	409
-10	14	375	408
-8	14	120	121
-4	14	243	246
-2	14	393	407
0	14	254	253
4	14	99	86
6	14	219	230
8	14	228	216
10	14	87	78
-22	16	152	160
-20	16	245	253
-18	16	110	125
-16	16	50	20
-12	16	255	293
-10	16	229	280
-8	16	65	63
-4	16	158	180
-2	16	276	303
0	16	162	174
4	16	61	66
6	16	215	206
8	16	204	181
-18	18	99	85
-14	18	89	100
-12	18	233	258
-10	18	201	212
-8	18	35	43
-6	18	57	46
-4	18	182	185
-2	18	280	268
0	18	145	130
4	18	51	65
-14	20	112	105
-12	20	224	228
-10	20	142	151
-6	20	57	49
-4	20	172	163
-2	20	191	188
K = 1			
5	0	93	98
7	0	75	75
9	0	36	4
13	0	63	48
15	0	48	24
-25	1	44	45
-21	1	128	97
-19	1	427	365
-17	1	347	301
-15	1	48	26
-11	1	543	549
-9	1	832	847
-7	1	516	481
-5	1	221	208
5	1	54	56
7	1	381	392
9	1	603	626
11	1	294	299
13	1	36	7
15	1	62	63
17	1	275	264
19	1	301	270
21	1	72	48
23	1	40	35
-11	2	72	57
-9	2	153	136
-7	2	107	88
-5	2	132	106
5	2	174	134
7	2	41	21
9	2	74	77
15	2	40	3
17	2	51	31
-25	3	49	28
-23	3	63	69
-19	3	434	400
-17	3	316	294
-15	3	60	51
-13	3	69	52
-11	3	559	535
-9	3	771	733
-7	3	307	293
-5	3	282	209
3	3	136	140
5	3	69	57
7	3	360	384
9	3	574	587
11	3	236	229
15	3	78	74
17	3	289	286
19	3	230	218
23	3	40	33
-23	4	75	10
-21	4	44	14
-19	4	50	58
-17	4	73	63
-15	4	41	15
-11	4	123	59
-9	4	139	121
-7	4	118	114
-5	4	109	113
-3	4	115	88
1	4	63	48
3	4	211	220
5	4	41	41
7	4	53	48
9	4	93	54
17	4	45	15
-21	5	147	173
-19	5	376	371
-17	5	215	218
-13	5	79	81
-11	5	341	341
-9	5	542	528
-7	5	216	205
-5	5	47	38
-3	5	295	276
-1	5	864	851
1	5	619	599
5	5	46	21
7	5	452	457
9	5	546	546
11	5	173	173
13	5	76	82
15	5	105	86
17	5	313	293
19	5	221	191
-21	6	64	28
-13	6	46	1
-11	6	99	34
-5	6	172	164
-3	6	40	19
-1	6	202	101
1	6	98	87
3	6	50	38
5	6	35	15
9	6	66	8
-23	7	56	30
-21	7	200	191
-19	7	371	360
-17	7	187	176
-15	7	71	77
-13	7	166	139
-11	7	541	509
-9	7	592	567
-7	7	165	153
-5	7	102	90
-3	7	421	384
-1	7	818	791
1	7	405	386
3	7	44	43
5	7	61	66
7	7	365	380
9	7	405	420
11	7	96	101
15	7	88	94
17	7	268	252
19	7	149	147
-23	8	46	6
-21	8	72	14
-17	8	66	7
-13	8	57	42
-11	8	46	34
-9	8	102	100
-5	8	119	124
1	8	101	45
3	8	44	80
5	8	49	64
7	8	43	11
13	8	39	5
-23	9	45	17
-21	9	226	210
-19	9	360	343
-17	9	121	117
-15	9	70	73
-13	9	168	167
-11	9	560	574
-9	9	453	470
-7	9	36	39
-5	9	56	52
-3	9	341	352
-1	9	601	614
1	9	275	267
3	9	70	74
5	9	122	111
7	9	379	388
9	9	338	341
11	9	76	64
13	9	61	39
15	9	110	94
17	9	213	196
19	9	99	94
-21	10	74	25
-17	10	40	1
-13	10	47	50
-11	10	46	55
-9	10	51	60
-5	10	82	104
-3	10	87	21
-1	10	144	45
1	10	71	74
3	10	64	38
5	10	38	31
-21	11	222	234
-19	11	298	365
-17	11	86	68
-15	11	37	54
-13	11	176	183
-11	11	417	471
-9	11	327	360
-7	11	33	27
-5	11	38	29
-3	11	374	395
-1	11	533	548
1	11	185	179
3	11	72	83
5	11	139	131
7	11	419	399
9	11	248	242
11	11	49	12
15	11	113	176
17	11	164	147
-15	12	40	24
-11	12	61	51
-7	12	48	65
-5	12	64	60
-3	12	95	49
-1	12	115	32
1	12	40	38
13	12	37	15
-23	13	43	35
-21	13	200	236
-19	13	237	262
-17	13	49	34
-15	13	59	60
-13	13	176	180
-11	13	393	441
-9	13	254	278
-5	13	47	38
-3	13	358	364
-1	13	395	406
1	13	102	113
3	13	74	74
5	13	94	90
7	13	244	277
9	13	162	162
-17	14	42	0
-3	14	86	27
-1	14	85	34
-21	15	160	214
-19	15	156	190
-13	15	145	176
-11	15	284	342
-9	15	141	156
-5	15	63	59
-3	15	246	267
-1	15	216	251
1	15	60	62
3	15	38	42
5	15	85	90
7	15	172	194
9	15	123	113
-11	16	75	34
-3	16	69	18
-1	16	59	12
-19	17	83	133
-13	17	129	169
-11	17	199	258
-9	17	67	93
-7	17	45	46
-5	17	73	80
-3	17	223	238
-1	17	166	193
1	17	40	78
5	17	110	112
7	17	169	166
-15	18	59	2
-13	18	52	12
-3	18	51	23
-1	18	44	9
1	18	43	2
-15	19	48	9
-13	19	133	163
-11	19	168	212
-9	19	48	67
-7	19	51	41
-5	19	79	77
-3	19	192	203
-1	19	123	143
-11	20	50	13
K = 2			
6	0	86	79
8	0	465	499
10	0	320	331
12	0	86	84
14	0	242	250
16	0	67	51
18	0	239	241
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7	1	210	229
11	1	217	228
13	1	390	396
15	1	239	240
17	1	41	31
19	1	38	4
21	1	152	128
23	1	168	160
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-21	2	49	19
-17	2	39	28
-15	2	173	191
-13	2	218	206
-11	2	55	66
-7	2	169	152
-5	2	351	349
-3	2	213	183
-1	2	46	51
1	2	44	59
3	2	176	184
5	2	230	217
7	2	76	76
9	2	43	27
13	2	173	178
15	2	55	78
19	2	42	3
-23	3	200	190
-21	3	102	95
-17	3	90	80
-15	3	352	338
-13	3	439	410
-11	3	115	99
-9	3	48	44
-7	3	460	413
-5	3	569	523
-3	3	224	200
1	3	122	106
3	3	421	428
5	3	426	445
7	3	139	135
11	3	212	220
13	3	310	313
15	3	186	185
21	3	130	125
-23	4	112	94
-15	4	175	175
-13	4	233	219
-11	4	49	45
-9	4	80	71
-7	4	131	116
-5	4	307	268
-3	4	130	113
3	4	250	236
5	4	174	177
7	4	75	80
11	4	79	85
13	4	158	154
15	4	50	54
21	4	47	51
-23	5	194	192
-21	5	92	78
-17	5	129	98
-15	5	411	368
-13	5	430	378
-11	5	83	86
-7	5	304	353
-5	5	615	537
-3	5	339	304
1	5	129	130
3	5	398	384
5	5	496	518
7	5	81	129
11	5	230	242
13	5	288	295
15	5	146	140
-23	6	91	90
-19	6	60	16
-17	6	47	30
-15	6	156	148
-13	6	151	139
-7	6	211	194
-5	6	272	243
-3	6	175	160
-1	6	45	48
3	6	246	238
5	6	164	156
7	6	71	62
11	6	68	63
15	6	45	50
-23	7	179	175
-19	7	41	13
-17	7	72	116
-15	7	357	373
-13	7	362	331
-11	7	90	78
-9	7	95	85
-7	7	420	394
-5	7	513	487
-3	7	271	241
-1	7	68	63
1	7	216	216
3	7	455	464
5	7	394	384
7	7	85	79
9	7	43	36
11	7	218	233
13	7	257	266
15	7	109	114
17	7	44	5
19	7	55	31
-21	7	79	66
-23	8	67	73
-21	8	43	0
-17	8	99	72
-15	8	153	149
-13	8	113	108
-9	8	45	39
-7	8	220	209
-5	8	190	193
-3	8	157	135
-1	8	44	45
3	8	180	173
5	8	134	109
7	8	47	21
11	8	77	75
13	8	123	110
-23	9	163	158
-21	9	42	31
-17	9	189	175
-15	9	352	331
-13	9	250	235
-9	9	94	44
-7	9	433	413
-5	9	443	423
-3	9	106	105
-1	9	51	57
1	9	200	175
3	9	397	391
5	9	290	299
7	9	52	23
11	9	203	197
13	9	212	207
15	9	86	77
-23	10	71	64
-17	10	113	86
-15	10	200	170
-13	10	100	98
-9	10	47	29
-7	10	152	177
-5	10	190	157
-3	10	67	62
1	10	90	78
3	10	177	165
5	10	124	98
11	10	77	67
13	10	91	77
15	10	55	20
-23	11	158	141
-17	11	192	177
-15	11	377	340
-13	11	217	203
-9	11	90	81
-7	11	395	376
-5	11	404	381
-3	11	111	100
1	11	230	220
3	11	353	340
5	11	232	210
9	11	59	44
11	11	172	173
13	11	163	158
15	11	50	43
-23	12	61	55
-17	12	87	77
-15	12	146	145
-13	12	93	74
-11	12	57	63
-7	12	191	166
-5	12	173	150
-3	12	61	46
-1	12	37	47
1	12	74	72
3	12	152	146
5	12	118	79
11	12	55	47
13	12	71	56
-21	13	43	7
-17	13	189	190
-15	13	287	273
-13	13	172	153
-9	13	151	131
-7	13	351	338
-5	13	289	255
-3	13	64	52
1	13	206	198
3	13	294	282
5	13	150	173
9	13	48	49
11	13	127	131
-17	14	80	73
-15	14	107	110
-13	14	75	61
-9	14	48	46
-7	14	137	129
-5	14	121	119
3	14	103	107
5	14	58	48
7	14	44	20
-17	15	180	182
-15	15	201	203
-13	15	73	79
-9	15	121	116
-7	15	256	260
-5	15	172	169
1	15	158	156
3	15	213	209
5	15	105	85
9	15	55	46
-17	16	66	69
-15	16	87	92
-13	16	40	29
-9	16	54	46
-7	16	110	101
-5	16	70	70
1	16	46	49
3	16	71	72
5	16	42	76
-17	17	164	154
-15	17	164	161
-9	17	116	118
-7	17	225	207
-5	17	148	134
1	17	150	140
3	17	159	157
-15	18	61	63
-7	18	83	90
-5	18	70	41
1	18	80	54
-9	19	130	115
-7	19	198	178
-5	19	106	91
K = 6			
2	0	136	133
4	0	309	320
6	0	266	260
8	0	50	20
10	0	69	66
12	0	202	207
14	0	242	249
16	0	50	41
18	0	72	49
20	0	68	9
22	0	116	103
-22	1	71	37
-18	1	66	60
-14	1	120	121
-10	1	103	108
-8	1	46	17
-4	1	308	278
-2	1	61	70
0	1	135	124
2	1	29	20
4	1	113	153
6	1	185	175
8	1	74	79
10	1	100	103
12	1	50	45
14	1	113	115
16	1	51	26
18	1	65	53
20	1	45	20
22	1	62	49
-22	2	105	101
-18	2	44	42
-16	2	89	76
-14	2	275	273
-12	2	134	138
-10	2	175	158
-6	2	343	308
-4	2	413	362
-2	2	34	24
0	2	182	164
2	2	185	198
4	2	321	332
6	2	173	188
8	2	61	64
10	2	80	91
12	2	182	190
14	2	186	188
18	2	40	52
20	2	52	12
-22	3	51	39
-16	3	42	52
-14	3	154	156
-12	3	110	105
-10	3	55	69
-6	3	172	142
-4	3	215	229
-2	3	69	72
0	3	187	169
2	3	31	1
4	3	165	162
6	3	109	97
8	3	69	86
10	3	40	43
12	3	104	107
14	3	112	127
-22	4	77	74
-20	4	52	37
-16	4	86	105
-14	4	246	237
-12	4	77	61
-10	4	183	171
-8	4	35	25
-6	4	264	262
-4	4	354	330
0	4	143	141
2	4	161	154
4	4	294	291
6	4	129	149
8	4	67	64
12	4	164	170
14	4	168	171
-16	5	92	82
-14	5	149	140
-12	5	44	33
-10	5	97	98
-8	5	44	53
-6	5	171	152
-4	5	75	83
-2	5	92	100
2	5	119	118
4	5	182	185
6	5	47	25
8	5	85	101
12	5	94	92
14	5	96	92
18	5	46	50
-22	6	43	63
-20	6	53	52
-18	6	61	29
-16	6	156	144
-14	6	256	250
-12	6	40	46
-10	6	109	106
-8	6	59	35
-6	6	319	265
-4	6	246	244
0	6	75	82
2	6	196	191
4	6	234	255
6	6	148	100
8	6	77	70
12	6	161	168
14	6	145	143
-16	7	75	83
-14	7	147	142
-12	7	42	33
-10	7	113	100
-8	7	58	56

residuals linear in the logarithm of the individual scale factors.[8] [The over-all R factor for scaling was $\sim 10\%$ based on F^2.] As a final stage of the preliminary data processing, data were placed on an approximately absolute scale by means of a Wilson plot.

Elucidation and Refinement of the Structure

The three-dimensional Patterson synthesis,[9] $P(U, V, W)$, which had been sharpened such that the average intensity was independent of $\sin \theta$, showed only seven

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(8) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(9) All crystallographic procedures were carried out using CRYRM, an integrated set of crystallographic routines for the IBM 7094 written by R. E. Marsh and his coworkers at the California Institute of Tchnology.

TABLE I (*Continued*)

H	L	FO	FC
***************			
K = 6			
-6	7	189	171
-4	7	125	114
-2	7	64	59
0	7	56	52
2	7	118	109
4	7	173	172
6	7	33	22
8	7	93	96
12	7	86	92
14	7	79	66
-22	8	53	54
-16	8	156	160
-14	8	263	248
-10	8	114	112
-8	8	92	73
-6	8	296	282
-4	8	214	208
-2	8	105	93
0	8	68	67
2	8	219	217
4	8	239	246
6	8	79	70
8	8	77	76
12	8	142	147
14	8	104	104
-18	9	40	21
-14	9	107	115
-12	9	44	16
-10	9	66	51
-8	9	59	47
-6	9	172	156
-4	9	95	86
-2	9	61	67
0	9	50	52
2	9	105	101
4	9	161	157
6	9	56	16
8	9	55	72
12	9	86	79
14	9	49	49
16	9	51	26
-22	10	45	30
-20	10	56	48
-16	10	156	158
-14	10	197	187
-10	10	93	100
-8	10	120	118
-6	10	261	253
-4	10	172	162
-2	10	73	73
0	10	57	54
2	10	201	193
4	10	227	220
8	10	49	48
10	10	47	31
12	10	121	127
14	10	83	73
-20	11	53	30
-18	11	51	1
-16	11	81	82
-14	11	63	72
-8	11	81	78
-6	11	164	137
-4	11	47	35
-2	11	49	57
0	11	44	31
2	11	84	82
4	11	92	93
6	11	44	10
8	11	81	60
12	11	40	53
-20	12	61	52
-16	12	163	170
-14	12	130	146
-12	12	49	36
-10	12	65	65
-8	12	126	128
-6	12	238	225
-4	12	96	86
-2	12	48	53
2	12	173	169
4	12	151	156
6	12	59	0
10	12	40	56
12	12	111	106
-20	13	68	37
-18	13	40	7
-16	13	79	89
-14	13	82	66
-12	13	48	31
-8	13	80	72
-6	13	140	121
-2	13	45	48
0	13	39	39
2	13	68	65
6	13	60	27
-16	14	133	149
-14	14	93	104
-12	14	65	63
-8	14	133	125
-6	14	173	171
-2	14	68	57
2	14	135	142
4	14	90	99
-16	15	89	87
-10	15	59	31
-8	15	68	54
-6	15	106	89
-4	15	44	13
-2	15	55	53
2	15	73	64
-16	16	106	118
-14	16	73	65
-12	16	54	54
-8	16	117	118
-6	16	138	130
-2	16	56	47
2	16	130	119
4	16	80	71
-16	17	58	65
-10	17	52	20
-6	17	50	55
2	17	53	60
-12	18	46	34
-8	18	100	96
-6	18	104	104
***************			
K = 7			
1	0	191	192
3	0	26	4
5	0	96	87
7	0	97	46
9	0	214	207
11	0	124	136
13	0	62	35
17	0	64	52
19	0	106	95
21	0	48	19
-19	1	117	98
-17	1	89	71
-13	1	77	76
-11	1	156	138
-9	1	278	261
-5	1	84	113
-1	1	329	275
1	1	274	251
3	1	116	144
5	1	121	135
7	1	111	114
9	1	247	248
11	1	91	87
13	1	83	86
15	1	46	47
17	1	94	92
19	1	78	84
-19	2	108	93
-11	2	120	113
-9	2	193	172
-5	2	146	127
-1	2	228	169
1	2	189	169
3	2	50	52
5	2	109	130
9	2	183	187
11	2	66	65
13	2	53	42
17	2	66	54
19	2	77	72
-21	3	53	23
-19	3	163	126
-15	3	54	58
-11	3	232	199
-9	3	298	251
-5	3	117	101
-3	3	70	68
-1	3	320	260
1	3	205	180
3	3	70	49
5	3	119	118
7	3	137	138
9	3	237	241
11	3	89	75
13	3	53	60
17	3	100	88
19	3	79	74
-19	4	84	86
-17	4	50	48
-15	4	73	83
-13	4	66	67
-11	4	138	121
-9	4	183	172
-5	4	171	162
-1	4	275	217
1	4	122	105
3	4	116	113
5	4	102	104
7	4	103	102
9	4	163	165
17	4	58	70
19	4	77	57
-19	5	125	118
-17	5	58	61
-15	5	64	68
-11	5	245	205
-9	5	241	209
-5	5	165	129
-3	5	79	60
-1	5	352	290
1	5	182	143
3	5	77	72
5	5	76	61
7	5	147	136
9	5	198	189
11	5	52	32
13	5	63	72
17	5	85	77
-19	6	117	87
-17	6	46	41
-15	6	52	65
-11	6	157	143
-9	6	178	149
-7	6	232	149
-5	6	115	104
-3	6	71	45
-1	6	221	183
1	6	138	131
3	6	57	52
5	6	52	71
7	6	130	115
9	6	160	155
13	6	53	45
15	6	45	4
17	6	79	76
-21	7	94	58
-19	7	99	105
-15	7	69	56
-11	7	219	191
-7	7	122	49
-5	7	137	99
-3	7	103	92
-1	7	265	221
1	7	150	119
3	7	101	99
5	7	69	61
7	7	163	136
9	7	162	149
13	7	75	72
17	7	88	77
-21	8	83	45
-19	8	79	80
-15	8	75	68
-13	8	49	34
-11	8	146	128
-9	8	107	91
-7	8	54	36
-5	8	82	77
-3	8	60	62
-1	8	189	147
1	8	85	64
7	8	118	111
9	8	120	102
-21	9	84	65
-19	9	104	104
-11	9	197	192
-9	9	182	161
-7	9	74	45
-5	9	79	73
-3	9	144	124
-1	9	199	174
1	9	62	52
3	9	85	77
7	9	156	142
9	9	132	125
13	9	70	55
-19	10	58	77
-15	10	85	82
-11	10	158	142
-9	10	104	88
-7	10	83	64
-5	10	74	71
-3	10	97	84
-1	10	177	143
3	10	106	74
7	10	130	112
9	10	83	75
-21	11	89	82
-19	11	96	96
-15	11	70	63
-11	11	199	181
-9	11	113	113
-7	11	69	77
-5	11	69	54
-3	11	142	121
-1	11	179	156
3	11	64	62
7	11	132	112
9	11	86	78
-19	12	91	72
-15	12	48	60
-11	12	126	119
-9	12	113	83
-7	12	59	37
-5	12	46	46
-3	12	95	75
-1	12	145	118
3	12	75	52
5	12	66	2
7	12	123	100
9	12	83	68
-19	13	71	77
-15	13	43	47
-13	13	51	40
-11	13	139	142
-9	13	91	80
-7	13	69	65
-5	13	59	15
-3	13	127	114
-1	13	136	115
3	13	77	63
5	13	46	76
7	13	81	88
9	13	60	41
-15	14	56	49
-11	14	89	88
-9	14	60	44
-5	14	53	34
-3	14	79	68
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1	14	50	11
3	14	69	41
7	14	75	75
-13	15	80	61
-11	15	115	119
-9	15	51	40
-7	15	70	52
-3	15	106	95
-1	15	106	79
3	15	81	45
-11	16	92	76
-5	16	47	12
-3	16	93	67
-1	16	62	69
1	16	43	3
-13	17	71	57
-11	17	97	94
-7	17	53	50
-3	17	67	76
-1	17	81	61
***************			
K = 8			
2	0	224	251
4	0	51	71
6	0	104	120
8	0	243	269
10	0	209	219
12	0	65	67
16	0	84	97
18	0	147	153
20	0	69	80
-20	1	101	88
-18	1	135	124
-12	1	62	74
-10	1	209	207
-8	1	212	209
-6	1	47	46
-2	1	157	150
0	1	346	288
2	1	170	190
8	1	191	213
10	1	184	195
12	1	38	42
16	1	41	65
18	1	115	126
20	1	65	64
-20	2	98	94
-18	2	148	151
-16	2	82	87
-12	2	128	128
-10	2	270	266
-8	2	264	247
-6	2	87	77
-4	2	52	55
-2	2	301	281
0	2	402	336
2	2	147	135
6	2	107	121
8	2	225	232
10	2	196	216
12	2	58	45
14	2	56	2
16	2	86	100
18	2	113	130
-20	3	81	91
-18	3	125	122
-12	3	76	68
-10	3	215	206
-8	3	196	201
-4	3	42	53
-2	3	192	164
0	3	286	241
2	3	135	138
4	3	37	24
8	3	173	206
10	3	137	151
16	3	65	54
18	3	100	109
-20	4	110	123
-18	4	148	150
-16	4	61	65
-12	4	137	146
-10	4	267	274
-8	4	228	207
-6	4	37	17
-4	4	64	50
-2	4	266	242
0	4	343	300
2	4	130	116
6	4	137	148
8	4	216	221
10	4	166	187
16	4	96	99
18	4	96	113
-20	5	104	107
-18	5	121	120
-14	5	47	42
-12	5	101	94
-10	5	222	218
-8	5	166	162
-2	5	209	188
0	5	248	210
2	5	107	96
4	5	39	21
6	5	79	78
8	5	162	171
10	5	98	118
12	5	53	28
-20	6	142	130
-18	6	153	147
-12	6	138	139
-10	6	255	229
-8	6	209	195
-6	6	33	39
-4	6	89	81
-2	6	285	238
0	6	309	274
2	4	94	98
4	6	46	49
6	6	136	128
8	6	205	213
10	6	136	150
12	6	49	13
16	6	92	94
-20	7	110	118
-18	7	118	112
-12	7	121	119
-10	7	221	219
-8	7	126	140
-6	7	34	0
-4	7	42	50
-2	7	256	222
0	7	224	194
2	7	36	36
6	7	102	103
8	7	171	176
10	7	87	90
-20	8	148	127
-18	8	133	127
-12	8	146	153
-10	8	260	230
-8	8	162	139
-6	8	50	38
-4	8	111	98
-2	8	276	243
0	8	271	234
2	8	50	47
4	8	39	46
6	8	137	127
8	8	181	179
10	8	106	115
-20	9	108	110
-18	9	94	95
-12	9	138	128
-10	9	199	181
-8	9	125	115
-2	9	215	181
0	9	208	181
2	9	47	38
6	9	78	73
8	9	156	153
10	9	88	86
-20	10	130	128
-18	10	118	115
-12	10	165	155
-10	10	237	220
-8	10	111	93
-4	10	106	91
-2	10	252	239
0	10	201	187
6	10	144	126
8	10	158	154
10	10	80	68
-18	11	86	75
-14	11	39	10
-12	11	146	132
-10	11	160	153
-8	11	102	67
-4	11	68	51
-2	11	184	161
0	11	166	146
2	11	57	42
6	11	89	78
8	11	126	113
10	11	61	63
-18	12	92	96
-14	12	52	44
-12	12	162	152
-10	12	190	175
-8	12	98	75
-4	12	121	101
-2	12	212	193
0	12	146	130
4	12	60	36
6	12	108	103
8	12	124	115
-18	13	62	54
-16	13	45	23
-12	13	130	127
-10	13	148	137
-4	13	73	61
-2	13	162	141
0	13	120	113
6	13	88	74
8	13	100	93
-14	14	53	52
-12	14	159	147
-10	14	146	134
-8	14	41	39
-4	14	111	101
-2	14	160	152
0	14	74	79
4	14	55	29
6	14	91	86
-12	15	106	106
-10	15	127	113
-8	15	66	28
-4	15	58	52
-2	15	121	113
0	15	74	69
-12	16	115	122
-10	16	102	102
-4	16	86	82
-2	16	137	123
0	16	81	60
***************			
K = 9			
1	0	243	255
3	0	119	130
5	0	40	37
7	0	146	150
9	0	209	197
11	0	134	132
17	0	105	100
19	0	126	117
-19	1	129	124
-17	1	138	127
-15	1	53	52
-13	1	59	59
-11	1	145	135
-9	1	237	225
-7	1	184	179
-5	1	62	81
-3	1	181	160
-1	1	325	269
1	1	271	244
3	1	110	102
5	1	62	61
7	1	193	197
9	1	215	221
11	1	108	101
13	1	54	30
15	1	57	51
17	1	122	128
-19	2	129	121
-17	2	108	106
-13	2	45	25
-11	2	149	154
-9	2	216	208
-7	2	139	146
-3	2	111	97
-1	2	299	260
1	2	227	215
3	2	39	22
7	2	124	127
9	2	179	183
11	2	99	99
17	2	84	98
-19	3	144	137
-17	3	127	115
-13	3	54	66
-11	3	172	157
-9	3	245	228
-7	3	151	132
-5	3	55	39
-3	3	188	159
-1	3	332	264
1	3	258	215
3	3	74	73
5	3	44	40
7	3	184	172
9	3	188	188
11	3	94	94
13	3	47	29
15	3	69	50
17	3	122	113
-19	4	139	131
-17	4	96	103
-11	4	157	149
-9	4	224	212
-7	4	97	75
-3	4	111	92
-1	4	288	245
1	4	230	208
3	4	31	21
7	4	156	161
9	4	165	173
11	4	74	73
15	4	55	39
-19	5	139	141
-17	5	108	95
-13	5	65	69
-11	5	177	165
-9	5	228	214
-7	5	117	103
-5	5	39	37
-3	5	168	144
-1	5	293	236
1	5	234	188
3	5	91	99
5	5	80	61
7	5	171	154
9	5	158	151
11	5	88	85
13	5	49	37
15	5	64	65
-19	6	129	136
-17	6	89	89
-13	6	61	44
-11	6	163	148
-9	6	194	181
-7	6	85	67
-3	6	148	131
-1	6	268	229
1	6	212	176
3	6	54	40
7	6	145	144
9	6	164	157
11	6	60	51
-19	7	152	136
-17	7	105	83
-15	7	51	31
-13	7	100	70
-11	7	179	173
-9	7	223	199
-7	7	101	81
-5	7	59	35
-3	7	212	171
-1	7	290	234
1	7	191	158
3	7	60	52
5	7	88	74
7	7	173	164
9	7	159	142
11	7	68	53
-19	8	127	117
-17	8	74	57
-15	8	54	1
-11	8	188	168
-9	8	175	151
-7	8	58	43
-3	8	165	137
-1	8	249	208
1	8	140	117
5	8	45	45
7	8	136	127
9	8	139	127
11	8	54	36
-19	9	150	126
-17	9	98	66
-13	9	98	76
-11	9	206	170
-9	9	208	181
-7	9	83	70
-5	9	38	31
-3	9	199	160
-1	9	245	203
1	9	163	143
5	9	64	61
7	9	155	138
9	9	136	122
-17	10	54	39
-13	10	65	66
-11	10	179	164
-9	10	164	140
-3	10	162	139
-1	10	227	183
1	10	110	74
5	10	44	48
7	10	136	122
9	10	111	98
-17	11	71	53
-15	11	51	23
-13	11	94	89
-11	11	179	163
-9	11	178	148
-7	11	56	47
-5	11	67	51
-3	11	201	158
-1	11	199	167
1	11	96	90
3	11	59	45
5	11	75	73
7	11	126	115
9	11	96	85
-13	12	83	70
-11	12	157	143
-9	12	138	118
-3	12	147	126
-1	12	183	154
1	12	52	59
7	12	113	102
-13	13	112	92
-11	13	152	143
-9	13	110	105
-5	13	64	58
-3	13	178	144
-1	13	165	131
1	13	62	53
5	13	85	62
-13	14	73	68
-11	14	125	120
-9	14	96	83
-3	14	124	104
-1	14	146	115
-11	15	116	112
-9	15	84	70
-5	15	47	49
-3	15	131	115
-1	15	128	99
***************			
K = 10			
2	0	103	106
4	0	32	9
6	0	36	50
8	0	115	125
10	0	121	124
12	0	49	50
14	0	60	2
-10	1	122	138
[illegible]	1	126	124
-2	1	111	118
0	1	238	229
2	1	99	118
4	1	39	45
8	1	114	122
10	1	118	135
12	1	37	21
-16	2	52	37
-14	2	46	3
-12	2	50	57
-10	2	104	113
-8	2	95	101
-2	2	133	123
0	2	192	161
2	2	90	83
8	2	99	111
10	2	92	95
-18	3	90	83
-12	3	63	63
-10	3	130	138
-8	3	110	118
-2	3	122	121
0	3	196	190
2	3	78	80
4	3	49	39
8	3	87	121
10	3	97	114
14	3	45	35
-18	4	85	73
-12	4	73	70
-10	4	120	117
-8	4	92	86
-6	4	45	2
-2	4	160	141
0	4	190	159
2	4	45	36
8	4	99	109
10	4	70	83
-18	5	89	86
-12	5	65	69
-10	5	144	152
-8	5	72	87
-6	5	44	39
-4	5	42	11
-2	5	164	155
0	5	190	176
6	5	47	53
8	5	97	114
10	5	69	90
12	5	41	4
-18	6	52	69
-12	6	85	73
-10	6	129	121
-8	6	90	94
-2	6	148	116
0	6	180	146
2	6	47	48
6	6	45	47
8	6	101	106
10	6	83	82
-12	7	62	72
-10	7	128	138
-8	7	67	68
-2	7	154	146
0	7	173	157
4	7	33	39
6	7	41	57
8	7	104	109
10	7	60	69
12	7	38	12
-16	8	46	3
-12	8	82	73
-10	8	110	102
-8	8	75	71
-2	8	152	120
0	8	126	112
2	8	37	35
6	8	65	52
8	8	99	94
10	8	53	55
-12	9	85	77
-10	9	112	117
-8	9	40	49
-4	9	39	29
-2	9	139	135
0	9	137	122
4	9	44	28
6	9	42	55
8	9	95	97
10	9	52	47
-12	10	100	75
-10	10	114	105
-8	10	48	50
-2	10	146	123
0	10	91	86
4	10	38	11
6	10	73	60
8	10	93	78
-12	11	102	85
-10	11	103	102
-8	11	41	25
-4	11	59	32
-2	11	124	118
0	11	105	98
6	11	74	43
-12	12	82	74
-10	12	96	90
-4	12	48	48
-2	12	118	102
0	12	85	63
-12	13	83	79
-10	13	97	90
-6	13	39	13
-2	13	95	94
0	13	57	66
-4	14	56	45
-2	14	100	80
***************			
K = 11			
1	0	47	52
3	0	35	47
5	0	59	57
9	0	43	58
11	0	45	27
13	0	55	56
15	0	55	55
-15	1	42	78
-5	1	71	60
-3	1	30	28
-1	1	47	44
1	1	36	76
3	1	43	36
5	1	59	47
9	1	61	59
-15	2	65	58
-13	2	63	53
-9	2	70	72
-5	2	98	87
-3	2	30	39
-1	2	85	95
1	2	56	59
3	2	83	87
5	2	79	87
9	2	46	71
13	2	50	61
-15	3	43	27
-13	3	47	32
-5	3	67	55
-3	3	30	19
-1	3	59	52
1	3	37	14
3	3	64	50
5	3	45	49
-13	4	42	47
-9	4	83	77
-5	4	101	97
-3	4	42	42
-1	4	97	97
1	4	57	53
3	4	75	85
5	4	70	78
9	4	50	65
11	4	45	1
-15	5	45	34
-13	5	41	15
-5	5	60	48
3	5	63	47
5	5	50	39
7	5	44	29
-15	6	66	57
-13	6	46	32
-11	6	49	57
-9	6	52	55
-7	6	59	44
-5	6	87	87
-1	6	64	72
1	6	34	29
3	6	73	66
5	6	44	49
9	6	66	47
-15	7	55	37
-7	7	34	23
-5	7	60	53
-1	7	55	43
1	7	35	1
3	7	60	44
-11	8	45	63
-7	8	68	54
-5	8	90	82
-3	8	40	10
-1	8	78	73
3	8	62	57
-11	9	47	72
-7	9	54	20
-5	9	54	40
-1	9	42	34
3	9	52	46
7	9	46	36
-11	10	46	64
-9	10	47	35
-7	10	64	53
-5	10	69	62
-1	10	53	61
3	10	74	59
-11	11	61	22
-1	12	43	42
***************			
K = 12			
2	0	43	59
4	0	51	75
6	0	32	45
12	0	39	40
-12	1	14	65
-6	1	53	95
-4	1	83	133
-2	1	48	66
0	1	19	5
2	1	48	61
4	1	68	126
6	1	70	91
12	1	58	72
-12	2	45	41
-6	2	64	65
-4	2	60	79
-2	2	39	49
2	2	52	61
4	2	63	83
4	2	35	36
-6	3	74	100
-4	3	98	118
-2	3	33	38
2	3	50	60
4	3	90	111
6	3	56	68
-6	4	68	68
-4	4	75	72
-2	4	39	36
2	4	39	57
4	4	61	75
6	4	34	38
-6	5	103	113
-4	5	106	114
2	5	71	80
4	5	99	109
-6	6	69	59
-4	6	65	64
0	6	46	9
2	6	66	54
4	6	66	62
-6	7	109	109
-4	7	96	96
0	7	35	10
2	7	55	86
4	7	90	101
-8	8	58	41
-6	8	74	60
-4	8	74	55
-2	8	49	32
2	8	68	49
4	8	50	53
-8	9	47	46
-6	9	118	103
-4	9	91	70
-2	9	47	3
2	9	66	73
-6	10	63	59
-4	10	39	46
-2	10	46	15
***************			
K = 13			
5	0	99	127
1	0	32	50
3	0	91	107
5	0	120	127
7	0	61	74
-7	1	58	45
-5	1	60	71
-3	1	58	61
-1	1	35	43
1	1	32	39
3	1	54	57
5	1	58	68
7	1	69	64
-7	2	85	82
-5	2	122	128
-3	2	97	94
-1	2	31	25
1	2	55	43
3	2	103	110
5	2	113	120
7	2	56	56
-7	3	54	51
-5	3	64	68
-3	3	60	56
-1	3	29	35
1	3	43	42
3	3	43	57
5	3	69	55
-7	4	93	82
-5	4	132	125
-3	4	91	75
-1	4	27	8
1	4	55	40
3	4	123	111
5	4	121	116
-7	5	80	58
-5	5	72	62
-3	5	60	47
-1	5	36	30
1	5	36	38
3	5	73	58
-5	6	140	122
-3	6	79	62
-1	6	41	16
1	6	55	54
-3	7	62	44
-3	7	62	44

[a] Table shows h, l, $|F_o|$, and $|F_c|$ in blocks of constant k.

independent peaks of sufficient magnitude to be attributable to rhenium···rhenium interactions.

A search of the Harker line 0, V, $^1/_2$ (for peaks of the type 0, $\pm 2y$, $^1/_2$) and the Harker section U, 0, W (for the peaks $\pm 2x$, 0, $^1/_2 \pm 2z$) failed to reveal an internally consistent pair of rhenium atom positions that could account successfully for all major peaks on the Patterson map. It was at this particular juncture that suspicions regarding the formulation of the complex as $[(n\text{-}C_4H_9)_4N][HRe_2(CO)_9]$ were really aroused. It now seemed probable that the rhenium anion might contain more than two rhenium atoms. Accordingly, the Patterson map was scanned for peaks located at ~3 Å from the origin, since they would be indicative of Re–Re or Re–(H)–Re bonds. [The rhenium–rhenium bond length in $Re_2(CO)_{10}$ is ~3.02 Å,[10] and the rhenium··· rhenium distance in $(OC)_5Re\text{–}H\text{–}ReMn(CO)_9$ is 3.39 Å.[1,11]] Two independent peaks of this nature were quickly found. This suggested the presence of three rhenium atoms in a triangular arrangement. Further examination of the Patterson map established that two of the rhenium atoms [Re_1 (0.00, 0.13, 0.25) and Re_2 (0.00, 0.35, 0.25)] had to lie on a twofold rotation axis. This requirement, in turn, indicated that the third rhenium atom [Re_3 (0.11, 0.24, 0.26)] must generate a fourth rhenium atom [Re_3* (−0.11, 0.24, 0.24)] as its symmetry-related mate. This arrangement of a cluster of four metal atoms was found to be consistent with the observed Patterson synthesis, both as regards the position *and* the height (strictly, of course, the volume) of the vector peaks; further it was now clear that the rhenium atom framework (at least) was consistent with the centrosymmetric space group C2/c. All subsequent calculations were performed in this space group, and the successful solution of the crystal structure (*vide infra*) indicates that this is, indeed, the correct choice. The asymmetric unit of the crystal structure thus consists of half of a tetranuclear rhenium dianion and a single tetra-*n*-butylammonium cation.

The initial structure factor calculation,[9] phased by rhenium atoms only, had the discrepancy index R_F = 0.32.[12] A difference-Fourier synthesis[9] quickly re-

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[10] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

[11] H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 2775 (1967).

[12] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w F_o^4$.

vealed the positions of eight crystallographically independent carbonyl ligands, indicating that the tetranuclear rhenium anion was probably $Re_4(CO)_{16}^{2-}$. No attempt was yet made to locate the atoms of the tetra-*n*-butylammonium cation, although its approximate location was already clear. Two cycles of refinement[9] of positions and isotropic thermal parameters for the rhenium atoms and the constituent atoms of the carbonyl ligands led to a reduction in the unweighted discrepancy index from $R_F = 0.288$ to 0.190. A second difference-Fourier synthesis now revealed the positions of all nonhydrogen atoms in the $(n\text{-}C_4H_9)_4N^+$ cation, except for C_{20} which was rather ill defined. An approximate position for C_{20} was found from a third difference-Fourier map, which was phased by all nonhydrogen atoms other than C_{20}. Four cycles of refinement of positional and individual isotropic thermal parameters for all 36 nonhydrogen atoms now reduced the discrepancy index to $R_F = 0.113$ ($R_{wF^2} = 0.061$).[12] At this stage it was noticed that the thermal parameters for atoms C_{19} and C_{20} had assumed unreasonable values and that the geometry around these centers was equally disturbing. A high-resolution difference-Fourier map, phased by all nonhydrogen atoms other than C_{19} and C_{20}, showed very diffuse peaks in the vicinity where these two carbon atoms were expected, indicating that they were disordered. [A careful survey of this difference-Fourier map did not suggest any simple alternative positions for C_{19} and C_{20}.] Attempts to refine the positional parameters of these atoms were unsuccessful, so it was finally decided to reset their coordinates at the positions of the maxima on the two diffuse peaks and to hold these two atoms at fixed positions during subsequent refinement procedures. [Disorder of this one terminal CH_2–CH_3 group in the tetra-*n*-butylammonium ion is discussed later in this text.]

As a final stage of the refinement process, the thermal parameters for rhenium atoms were allowed to refine anisotropically. After seven cycles of refinement of anisotropic thermal parameters for rhenium atoms, isotropic thermal parameters for carbon, nitrogen, and oxygen atoms, and positional parameters for all atoms save C_{19} and C_{20}, no parameter was varying by more than one-tenth of the appropriate standard deviation. A difference-Fourier synthesis at this stage ($R_F = 0.1065$, $R_{wF^2} = 0.0574$) showed no peak of height greater than 1 $e^-/Å^3$ except in the vicinity of rhenium and oxygen atoms, and in the general region around C_{19} and C_{20}. [A final attempt to unravel the pattern of disorder for these two atoms was again unsuccessful.]

It was felt that the application of anisotropic thermal parameters for carbon, nitrogen, and oxygen atoms was ill advised since: (i) evidence (from difference-Fourier maps) for such motion was not well defined, (ii) the esd's on the isotropic parameters were already large, (iii) anisotropic refinement of rhenium atom thermal parameters had produced only a relatively small (although significant) improvement in R factor, and (iv) any possible advantages would be offset by the high cost of the process, which would take approximately 1 hr of IBM 7094 time per cycle. Refinement was therefore discontinued at this point. No attempt was made to locate hydrogen atoms on the $(n\text{-}C_4H_9)_4N^+$ ion.

Throughout the analysis, the scattering factors for neutral rhenium, oxygen, nitrogen, and carbon (as compiled by Ibers[13]) were used. A specific correction was applied for dispersion [$\Delta f'(\text{Re}) = -1.2\ e^-$, $\Delta f''(\text{Re}) = +8.0\ e^-$ for Mo Kα radiation].[14] The residual minimized during refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, and the final error in an observation of unit weight was 2.9 (indicating that the standard deviations of the intensity data have been underestimated).

The final observed and calculated structure factors are shown in Table I. Positional and thermal parameters for all atoms are collected in Table II.

Description of the Molecular Structure

Crystals of $[(n\text{-}C_4H_9)_4N]_2[Re_4(CO)_{16}]$ consist of individual tetra-*n*-butylammonium—$(n\text{-}C_4H_9)_4N^+$—cations and hexadecacarbonyltetrarhenium—$Re_4(CO)_{16}^{2-}$—dianions. Figure 1 depicts the structure projected on 010 and also gives the key to the numbering of atoms within both the anion and the cation. All important bond distances (with their appropriate esd's) are collected in Table III; bond angles (with esd's) are given in Table IV.

The over-all configuration of the $Re_4(CO)_{16}^{2-}$ ion is shown clearly in Figure 2. The four rhenium atoms are arranged as two fused, approximately equilateral triangles. A crystallographic twofold axis passing through Re_1 and Re_2 requires that the four rhenium atoms lie in a plane. The $Re_4(CO)_{16}^{2-}$ ion contains the first-reported planar, triangulated, tetranuclear cluster of metal atoms, thus adding another regular shape to the abundance of geometries (*viz.*, octahedron in $Rh_6(CO)_{16}$,[15] square pyramid in $Fe_5(CO)_{15}C$,[16] tetrahedron in $Ir_4(CO)_{12}$,[17] equilateral triangle in $Os_3(CO)_{12}$,[18] isosceles triangle in $Fe_3(CO)_{12}$[19]) that have been observed in metal–carbonyl clusters. [A fused, triangulated, tetranuclear cluster of cobalt atoms appears in the metal atom skeleton of $Co_4(CO)_{10}(C_2H_5C{\equiv}C\text{-}C_2H_5)$,[20] but there is a dihedral angle of 118° between the two three-membered rings in this complex.]

Individual rhenium–rhenium distances within the $Re_4(CO)_{16}^{2-}$ ion are: Re_1–Re_2 = 2.956 ± 0.007 Å, Re_1–Re_3 = 2.982 ± 0.007 Å, Re_2–Re_3 = 3.024 ± 0.007 Å, and $Re_3 \cdots Re_3^*$ = 5.227 ± 0.010 Å. The observation that the shortest of the bonding distances involves the triply bridging rhenium atoms (Re_1 and Re_2) is probably not chemically significant, since the chemically equivalent distances Re_1–Re_3 and Re_2–Re_3 differ by

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[13] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, pp 202–203, 211–212.

[14] See ref 13, p 217.

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TABLE II

(A) Final Atomic Parameters for $[(C_4H_9)_4N]_2[Re_4(CO)_{16}]^a$

Atom	x	y	z	B, Å^2
Re_1	0.00000^b	0.12364 (14)	0.25000^b	c
Re_2	0.00000^b	0.35228 (13)	0.25000^b	c
Re_3	0.10890 (6)	0.23465 (11)	0.26427 (7)	c
O_1	0.0879 (13)	−0.0511 (20)	0.2463 (15)	8.3 (7)
O_2	0.0403 (12)	0.1141 (19)	0.4177 (17)	8.4 (7)
O_3	0.0899 (10)	0.5251 (16)	0.2872 (12)	6.2 (5)
O_4	0.0058 (12)	0.3446 (18)	0.4119 (15)	7.8 (7)
O_5	0.2028 (13)	0.0703 (22)	0.3099 (16)	9.6 (8)
O_6	0.1327 (14)	0.2808 (22)	0.4263 (18)	9.7 (8)
O_7	0.1899 (12)	0.4077 (19)	0.2557 (14)	7.6 (6)
O_8	0.0874 (13)	0.1827 (22)	0.1026 (16)	9.5 (7)
N	0.1194 (12)	0.2842 (19)	0.6389 (14)	5.8 (6)
C_1	0.0563 (15)	0.0204 (23)	0.2505 (18)	6.1 (8)
C_2	0.0244 (17)	0.1266 (25)	0.3552 (21)	6.3 (8)
C_3	0.0605 (17)	0.4498 (26)	0.2763 (20)	6.9 (9)
C_4	0.0058 (17)	0.3472 (25)	0.3523 (22)	6.9 (9)
C_5	0.1674 (17)	0.1354 (26)	0.2912 (20)	6.6 (8)
C_6	0.1209 (15)	0.2667 (23)	0.3644 (20)	5.8 (7)
C_7	0.1600 (17)	0.3365 (27)	0.2565 (20)	6.7 (9)
C_8	0.0898 (17)	0.2020 (28)	0.1658 (21)	6.9 (9)
C_9	0.0627 (16)	0.2720 (24)	0.6616 (19)	6.4 (8)
C_{10}	0.0119 (27)	0.2362 (35)	0.6002 (32)	11.7 (15)
C_{11}	−0.0404 (22)	0.2231 (34)	0.6327 (26)	9.7 (12)
C_{12}	−0.0918 (24)	0.1799 (36)	0.5779 (27)	10.7 (13)
C_{13}	0.1325 (19)	0.1760 (31)	0.6150 (23)	8.3 (10)
C_{14}	0.1901 (19)	0.1726 (30)	0.5982 (22)	8.0 (10)
C_{15}	0.1878 (21)	0.0521 (33)	0.5596 (24)	8.9 (11)
C_{16}	0.2372 (31)	0.0455 (52)	0.5337 (36)	15.4 (20)
C_{17}	0.1141 (16)	0.3552 (26)	0.5711 (20)	6.7 (8)
C_{18}	0.0916 (20)	0.4658 (33)	0.5927 (25)	9.6 (12)
$C_{19}{}^d$	0.094	0.542	0.525	12.0
$C_{20}{}^d$	0.132	0.535	0.495	12.0
C_{21}	0.1641 (16)	0.3271 (25)	0.7009 (20)	6.7 (8)
C_{22}	0.1820 (17)	0.2478 (25)	0.7688 (21)	6.9 (8)
C_{23}	0.2285 (19)	0.2997 (32)	0.8236 (24)	8.5 (10)
C_{24}	0.2514 (26)	0.2527 (35)	0.8977 (32)	12.2 (16)

(B) Anisotropic Temperature Factors for Rhenium Atoms

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Re_1	22.7 (6)	73.1 (12)	37.6 (9)	0.0^b	27.0 (11)	0.0^b
Re_2	19.5 (5)	75.0 (13)	29.7 (8)	0.0^b	15.1 (10)	0.0^b
Re_3	18.2 (3)	100.8 (10)	33.4 (5)	4.9 (10)	19.1 (6)	8.4 (13)

(C) Thermal Vibration Ellipsoids for Rhenium Atoms^e

B_{max} (dc's, major axis)	B_{med} (dc's, median axis)	B_{min} (dc's, minor axis)
	Re_1 Atom	
5.72	4.88	3.93
(0.535, −0.203, 0.619)	(0.296, −0.951, 0.000)	(−0.709, −0.533, 0.655)
	Re_2 Atom	
5.01	4.29	4.06
(0.169, −0.984, 0.000)	(0.875, −0.345, 0.057)	(−0.349, −0.251, 0.966
	Re_3 Atom	
6.83	4.51	3.65
(0.078, 0.981, 0.146)	(0.354, −0.194, 0.764)	(−0.932, 0.008, 0.628)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and are right-adjusted to the least significant digit of the preceding number. [b] These parameters are required to be fixed by the space group symmetry. [c] See anisotropic parameters in part B of this table. [d] Atoms C_{19} and C_{20} were disordered and could not be refined. These parameters have been estimated from a difference-Fourier map. Isotropic thermal parameters have been fixed at B = 12 Å^2. [e] The thermal vibration ellipsoids are defined in terms of the isotropic thermal parameter B, which is related to the root-mean-square displacement, $(\overline{U^2})^{1/2}$, by $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$. The direction cosines (dc's) refer to the natural crystal axes—a, b, c.

~0.04 Å. This latter discrepancy perhaps arises as a combination of (i) asymmetry in the oxygen···oxygen repulsions between adjacent sets of carbonyl ligands (*vide infra*) and (ii) statistical errors in bond distance determination. In any case, each of the observed rhenium–rhenium bond lengths is close to the value of ~3.02 Å found for the rhenium–rhenium single bond in $Re_2(CO)_{10}$.[10] [It should be noted that the rhenium–rhenium distance of ~2.48 Å, found in trinuclear halogenated Re(III) complexes such as $Re_3Cl_{12}{}^{3-}$,[21–31] corresponds to a formal metal–metal bond order of 2;[32,33] and the rhenium–rhenium distance of ~2.24 Å in such ions as $Re_2Cl_8{}^{2-}$ [34–36] corresponds to a formal quadruple metal–metal bond.[34,36–37]]

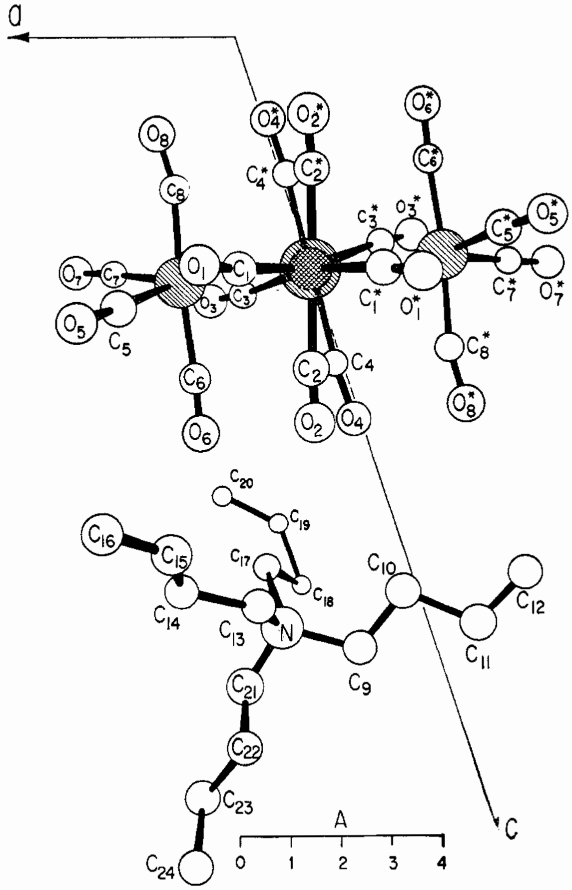

Figure 1.—The structure projected on 010. For the sake of clarity, rhenium–rhenium bonds have not been drawn in. Atoms related to the basic asymmetric unit by the relationship $(-x, y, {}^1/_2 - z)$ are marked with an asterisk.

As is usually the case for third-row transition metals, the $Re_4(CO)_{16}{}^{2-}$ ion contains no bridging carbonyl

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TABLE III

INTERATOMIC DISTANCES AND ESD'S FOR $[(C_4H_9)_4N]_2[Re_4(CO)_{16}]$ (ALL IN Å)[a]

(a) Metal–Metal Distances

Re_1-Re_2	2.956 (07)	Re_2-Re_3	3.024 (07)
Re_1-Re_3	2.982 (07)	$Re_3\cdots Re_3^*$	5.227 (10)

(b) Metal–Carbon Distances

Re_1-C_1	1.92 (3)	Re_3-C_5	1.88 (4)
Re_1-C_2	1.95 (4)	Re_3-C_6	1.93 (4)
Re_2-C_3	1.90 (4)	Re_3-C_7	1.86 (4)
Re_2-C_4	1.96 (3)	Re_3-C_8	1.88 (4)
		Re–C (av)	1.91

(c) Metal–Oxygen Distances

$Re_1\cdots O_1$	3.15 (3)	$Re_3\cdots O_5$	3.07 (3)
$Re_1\cdots O_2$	3.12 (2)	$Re_3\cdots O_6$	3.09 (3)
$Re_2\cdots O_3$	3.07 (2)	$Re_3\cdots O_7$	3.04 (3)
$Re_2\cdots O_4$	3.12 (2)	$Re_3\cdots O_8$	3.10 (3)
		Re···O(av)	3.09

(d) Carbon–Oxygen Distances

C_1-O_1	1.22 (4)	C_5-O_5	1.19 (5)
C_2-O_2	1.17 (5)	C_6-O_6	1.17 (4)
C_3-O_3	1.19 (4)	C_7-O_7	1.18 (5)
C_4-O_4	1.16 (4)	C_8-O_8	1.24 (5)
		C–O(av)	1.19

(e) Nonbonding Contacts

$O_1\cdots O_5$	3.14 (4)	$C_1\cdots C_5$	3.00 (6)
$O_2\cdots O_4$	3.09 (4)	$C_2\cdots C_4$	2.89 (4)
$O_2\cdots O_6$	3.10 (4)	$C_2\cdots C_6$	2.96 (5)
$O_3\cdots O_7$	3.11 (4)	$C_3\cdots C_7$	2.98 (6)
$O_4\cdots O_6$	3.16 (4)	$C_4\cdots C_6$	2.96 (5)
$O_8\cdots O_2^*$	3.18 (4)	$C_8\cdots C_2^*$	2.89 (6)
$O_8\cdots O_4^*$	3.06 (4)	$C_8\cdots C_4^*$	2.95 (5)

(f) Nitrogen–Carbon and Carbon–Carbon Distances

$N-C_9$	1.60 (5)	$N-C_{17}$	1.58 (4)
$N-C_{13}$	1.54 (5)	$N-C_{21}$	1.47 (4)
		N–C(av)	1.55
C_9-C_{10}	1.52 (7)	$C_{17}-C_{18}$	1.63 (5)
$C_{10}-C_{11}$	1.61 (9)	$C_{18}-C_{19}$	[1.66][b]
$C_{11}-C_{12}$	1.49 (7)	$C_{19}-C_{20}$	[1.25][b]
$C_{13}-C_{14}$	1.55 (7)	$C_{21}-C_{22}$	1.63 (5)
$C_{14}-C_{15}$	1.72 (7)	$C_{22}-C_{23}$	1.47 (6)
$C_{15}-C_{16}$	1.46 (9)	$C_{23}-C_{24}$	1.51 (7)
		C–C(av)	1.56[c]

[a] Esd's (in parentheses) are right-adjusted to the last digit of the preceding number. They include contributions from errors in cell constants. [b] Atoms C_{19} and C_{20} were disordered and could not be refined. These distances are based on positions estimated from a difference Fourier map (see text). [c] This average does not include $C_{18}-C_{19}$ or $C_{19}-C_{20}$.

TABLE IV

INTERATOMIC ANGLES (DEG) WITHIN THE $[(C_4H_9)_4N]_2[Re_4(CO)_{16}]$ MOLECULE[a]

(a) Angles between Metal Atoms

$Re_1-Re_2-Re_3$	59.80 (0.04)	$Re_3-Re_1-Re_2$	61.23 (0.04)
$Re_2-Re_3-Re_1$	58.96 (0.05)		

(b) Angles at Metal Atoms

$O_1-Re_1-Re_3$	75.0 (0.5)	$C_1-Re_1-Re_3$	72.9 (1.0)
$O_1-Re_1-Re_2$	135.9 (0.5)	$C_1-Re_1-Re_2$	133.9 (1.0)
$O_1-Re_1-Re_3^*$	161.9 (0.5)	$C_1-Re_1-Re_3^*$	164.2 (1.0)
$O_1-Re_1-O_1^*$	88.2 (0.7)	$C_1-Re_1-C_1^*$	92.1 (1.4)
$O_2-Re_1-O_1$	89.6 (0.7)	$C_2-Re_1-C_1$	90.9 (1.4)
$O_2-Re_1-Re_3$	86.0 (0.6)	$C_2-Re_1-Re_3$	84.9 (1.1)
$O_2-Re_1-Re_2$	92.3 (0.5)	$C_2-Re_1-Re_2$	88.9 (0.9)
$O_2-Re_1-Re_3^*$	96.2 (0.6)	$C_2-Re_1-Re_3^*$	94.0 (1.1)
$O_2-Re_1-O_1^*$	87.1 (0.8)	$C_2-Re_1-C_1^*$	90.6 (1.4)
$O_2-Re_1-O_2^*$	175.5 (0.7)	$C_2-Re_1-C_2^*$	177.8 (1.3)
$O_3-Re_2-Re_3$	77.8 (0.4)	$C_3-Re_2-Re_3$	72.9 (1.1)
$O_3-Re_2-Re_1$	136.6 (0.4)	$C_3-Re_2-Re_1$	131.6 (1.1)
$O_3-Re_2-Re_3^*$	160.6 (0.4)	$C_3-Re_2-Re_3^*$	163.8 (1.1)
$O_3-Re_2-O_3^*$	86.7 (0.6)	$C_3-Re_2-C_3^*$	96.9 (1.5)
$O_4-Re_2-O_3$	88.6 (0.6)	$C_4-Re_2-C_3$	86.5 (1.5)
$O_4-Re_2-Re_3$	97.2 (0.5)	$C_4-Re_2-Re_3$	95.8 (1.0)
$O_4-Re_2-Re_1$	88.2 (0.5)	$C_4-Re_2-Re_1$	88.1 (0.8)
$O_4-Re_2-Re_3^*$	81.0 (0.5)	$C_4-Re_2-Re_3^*$	82.2 (1.0)
$O_4-Re_2-O_3^*$	94.0 (0.6)	$C_4-Re_2-C_3^*$	96.1 (1.5)
$O_4-Re_2-O_4^*$	176.4 (0.7)	$C_4-Re_2-C_4^*$	176.2 (1.1)
$O_6-Re_3-Re_1$	94.3 (0.6)	$C_6-Re_3-Re_1$	93.1 (1.0)
$O_6-Re_3-Re_2$	83.4 (0.6)	$C_6-Re_3-Re_2$	81.0 (1.0)
$O_6-Re_3-O_7$	89.4 (0.8)	$C_6-Re_3-C_7$	91.8 (1.4)
$O_6-Re_3-O_5$	86.9 (0.8)	$C_6-Re_3-C_5$	89.7 (1.6)
$O_8-Re_3-Re_1$	86.0 (0.6)	$C_8-Re_3-Re_1$	81.9 (1.2)
$O_8-Re_3-Re_2$	98.2 (0.6)	$C_8-Re_3-Re_2$	94.6 (1.2)
$O_8-Re_3-O_7$	90.9 (0.8)	$C_8-Re_3-C_7$	92.3 (1.6)
$O_8-Re_3-O_5$	91.4 (0.8)	$C_8-Re_3-C_5$	93.7 (1.7)
$O_6-Re_3-O_8$	178.3 (0.9)	$C_6-Re_3-C_8$	174.6 (1.7)
$Re_1-Re_3-O_5$	105.8 (0.6)	$Re_1-Re_3-C_5$	106.8 (1.5)
$O_5-Re_3-O_7$	94.3 (0.8)	$C_5-Re_3-C_7$	91.4 (1.8)
$Re_2-Re_3-O_7$	101.8 (0.5)	$Re_2-Re_3-C_7$	104.0 (1.1)
$Re_1-Re_3-O_7$	159.7 (0.5)	$Re_1-Re_3-C_7$	161.1 (1.1)
$Re_2-Re_3-O_5$	161.0 (0.6)	$Re_2-Re_3-C_5$	162.2 (1.4)

(c) Re–C–O Angles

$Re_1-C_1-O_1$	174 (3)	$Re_3-C_5-O_5$	177 (4)
$Re_1-C_2-O_2$	171 (3)	$Re_3-C_6-O_6$	174 (3)
$Re_2-C_3-O_3$	167 (3)	$Re_3-C_7-O_7$	173 (3)
$Re_2-C_4-O_4$	176 (3)	$Re_3-C_8-O_8$	169 (4)

(d) Angles Associated with the $(C_4H_9)_4N^+$ Cation

C_9-N-C_{13}	106 (3)	$C_{13}-N-C_{17}$	104 (3)
C_9-N-C_{17}	116 (3)	$C_{13}-N-C_{21}$	115 (3)
C_9-N-C_{21}	108 (3)	$C_{17}-N-C_{21}$	109 (3)
$N-C_9-C_{10}$	113 (3)	$N-C_{17}-C_{18}$	104 (3)
$C_9-C_{10}-C_{11}$	107 (4)	$C_{17}-C_{18}-C_{19}$	[103][b]
$C_{10}-C_{11}-C_{12}$	111 (4)	$C_{18}-C_{19}-C_{20}$	[123][b]
$N-C_{13}-C_{14}$	112 (3)	$N-C_{21}-C_{22}$	112 (3)
$C_{13}-C_{14}-C_{15}$	102 (3)	$C_{21}-C_{22}-C_{23}$	105 (3)
$C_{14}-C_{15}-C_{16}$	106 (4)	$C_{22}-C_{23}-C_{24}$	120 (4)

[a] Angular esd's are shown in parentheses. [b] Atoms C_{19} and C_{20} were disordered and could not be refined. These angles are based on positions estimated from a difference-Fourier map (see text).

groups.[38,39] Each of the four rhenium atoms is associated with four terminal carbonyl ligands, two of which are approximately *axial* and two approximately *equatorial*. [The disposition of carbonyl ligands about each rhenium center is fairly regular. Since hydride ligands are now known to occupy regular coordination sites, the lack of large "holes" in the individual rhenium coordination spheres confirms that the anion is $Re_4(CO)_{16}^{2-}$, rather than $H_nRe_4(CO)_{16}^{2-}$ (n = integer). Considerations of the "noble gas rule" (below) are in keeping with this conclusion.]

The two triply bridging rhenium atoms (*i.e.*, Re_1 and Re_2) have distorted pentagonal-bipyramidal stereochemistries and may each be regarded as being in a zerovalent oxidation state; these d^7 Re(0) atoms then achieve the appropriate noble gas configuration (*i.e.*,

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(38) This results mainly from the inability for carbonyl ligands to bridge distances greater than ~2.8 Å. When a compound of a third-row element has metal–metal bond lengths less than this value, there is no reason for the "terminal only" rule, and in such cases (*e.g.*, $Ir_4(CO)_{10}[P(C_6H_5)_3]_2$[39]) bridging carbonyls are observed.

(39) V. Albano, P. Bellon, and A. Scatturin, *Chem. Commun.*, 730 (1967).

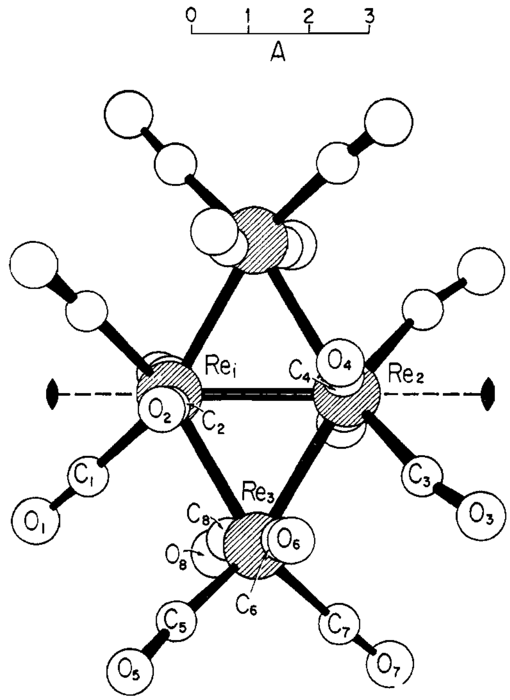

Figure 2.—The $Re_4(CO)_{16}^{2-}$ ion projected in the plane of the four rhenium atoms.

that of Rn) by obtaining one electron from each of three rhenium atoms and two electrons from each of the four associated terminal carbonyl ligands. The singly bridging rhenium atoms (Re_3 and Re_3*) may be regarded formally as Re(−1) ions having a d^8 configuration; the inert gas configuration is again achieved, this time by the metal atom obtaining one electron from each of two rhenium atoms and a total of eight electrons from the four terminal carbonyl groups. Thus, the two negative charges on the tetranuclear cluster are formally associated with the well-separated Re_3 and Re_3*. It seems probable, however, that a molecular orbital treatment of this rhenium cluster would show that the distinction between Re(0) and Re(−1) ions is not so clear-cut as that outlined above and that delocalization of the net negative charge over all four rhenium atoms would blur the formal distinction between zerovalent and uninegative metal centers.

A further interesting feature of the tetranuclear dianion is that the carbonyl groups adopt a skewed configuration relative to the plane of the four rhenium atoms. Thus, relative to imaginary axes drawn from the center of the metal cluster through each rhenium atom, each of the $Re(CO)_4$ groups is rotated in a clockwise manner. [The direction of rotation mentioned here refers to the molecule depicted in Figures 1 and 2; as discussed below, the direction of rotation varies from molecule to molecule.] As shown in Table V, this results (*inter alia*) in the equatorial carbonyl groups lying alternatively above and below the plane of the four rhenium atoms. Visual representation of the effect on *equatorial* carbonyl groups is available in Figure 1, while the clockwise rotation of the *axial* carbonyl groups is clearly demonstrated in Figure 2. A quantitative measure of the skewing may be obtained from the direction cosines (dc's) in Table VI, and it can be shown that the carbonyl groups on Re_1 have been rotated by 6° 21′, those on Re_2 by 11° 17′, and those on Re_3 (and Re_3*) by 12° 41′ relative to the idealized D_{2h} conformation. This effect is almost certainly the result of intramolecular repulsions. The rotation of the *axial* carbonyl ligands results in the relieving of oxygen···oxygen repulsions. If each of the axial carbonyl groups lay perpendicular to the plane of the four rhenium atoms, the oxygen···oxygen contacts would be identical with the observed rhenium–rhenium distances (*i.e.*, between 2.96 and 3.02 Å). As it is, the *axial* oxygen···oxygen contacts are increased to: $O_2 \cdots O_4 = 3.09$ Å, $O_2 \cdots O_6 = 3.10$ Å, $O_6 \cdots O_4 = 3.16$ Å, $O_4 \cdots O_8^* = 3.06$ Å, $O_8^* \cdots O_2 = 3.18$ Å—*i.e.*, by about 0.1 Å unit in each case. [The *equatorial* oxygen···oxygen contacts are also relieved by the skewing distortion.]

TABLE V

DISTANCES OF CARBON AND OXYGEN ATOMS FROM THE RHENIUM ATOM PLANE (WITH ESD'S)

Plane: $-0.1013X + 0.0000Y + 0.9948Z - 4.7681 - 0^a$

Atom	Dist, Å	Atom	Dist, Å
O_1	−0.29 (3)	C_1	−0.13 (4)
O_3	+0.49 (2)	C_3	+0.35 (4)
O_5	+0.63 (3)	C_5	+0.37 (4)
O_7	−0.37 (3)	C_7	−0.28 (4)
O_2	+3.10 (3)	C_2	+1.95 (4)
O_4	+3.07 (2)	C_4	+1.94 (4)
O_6	+3.03 (3)	C_6	+1.88 (4)
O_8	−3.03 (3)	C_8	−1.83 (4)

[a] The equation to the plane is expressed in Cartesian coordinates (*X*, *Y*, *Z*). These are related to the cell coordinates (*x*, *y*, *z*) by: $X = xa + zc\cos\beta$; $Y = yb$; $Z = zc\sin\beta$.

TABLE VI

DIRECTION COSINES FOR LEAST-SQUARES PLANES WITHIN THE $Re_4(CO)_{16}^{2-}$ ANION

Each Plane: $C_1X + C_2Y + C_3Z - d = 0^a$

	Plane	C_1	C_2	C_3	d
a	Re_1, Re_2, Re_3	−0.1013	0.0000	0.9948	4.7681
b	Re_1, Re_2, O_1, C_1, O_1*, C_1*	0.0204	0.0000	0.9997	4.6107
c	Re_1, Re_2, O_2, C_2, O_2*, C_2*	0.9999	0.0000	0.0027	−1.4684
d	Re_1, Re_2, O_3, C_3, O_3*, C_3*	−0.3322	0.0000	0.9432	4.8703
e	Re_1, Re_2, O_4, C_4, O_4*, C_4*	0.9670	0.0000	0.2546	−0.2499
f	Re_3, Re_3*, C_5, O_5, C_7, O_7	−0.1146	0.2277	0.9669	5.3672
g	Re_3, Re_3*, C_6, O_6, C_8, O_8	−0.0247	−0.9779	0.2074	−1.9578

[a] See footnote *a*, Table V.

The sterically forced deviation of the dianion from D_{2h} symmetry has another rather interesting result. That is, that the $Re_4(CO)_{16}^{2-}$ ion is not superposable on its mirror image and is therefore optically active. By virtue of the *c*-glide operation in space group C2/c, the present crystal contains equal numbers of molecules in which the $Re(CO)_4$ groups are rotated "clockwise" and "anticlockwise" with respect to the idealized D_{2h} conformation. However, in principle, it should be possible to separate the "clockwise" and "anticlockwise" optical isomers.

A final point of chemical interest concerns possible redox behavior of the $Re_4(CO)_{16}^{2-}$ anion. Thus, in both a tetrahedral $Re_4(CO)_{16}$ molecule and a square-planar $Re_4(CO)_{16}^{4-}$ anion, each metal atom would attain the appropriate noble gas configuration. It might be possible, therefore, for the known $Re_4(CO)_{16}^{2-}$ ion to undergo both a two-electron oxidation (to the tetrahedral neutral species) and a two-electron reduction (to the square-planar tetraanion). Experiments involving these and related reactions are presently in progress in the laboratories of Professor H. D. Kaesz.

The Tetra-*n*-butylammonium Cation

The over-all configuration of the tetra-*n*-butylammonium cation is shown in Figure 1. Three of the *n*-butyl limbs take up a *trans* conformation, while the fourth limb has a *gauche* conformation in which the terminal two carbon atoms may reasonably be assumed to be disordered. A survey of the thermal parameters of the carbon atoms within the tetra-*n*-butylammonium ion shows evidence of large amplitudes of thermal motion. [Mean isotropic thermal parameters are 7.0 Å^2 for α-carbon atoms, 9.1 Å^2 for β-carbons, 9.0 Å^2 for γ-carbons (neglecting C_{19}), and 12.8 Å^2 for δ-carbons (neglecting C_{20}).]

It should be emphasized that disorder of the terminal $-CH_2-CH_3$ group of a single *n*-butyl group has previously been reported for $[(n\text{-}C_4H_9)_4N]_2[Fe_2(S_2C_2(CN)_2)_4]$,[40] and disorder of a single terminal methyl group probably occurs in $[(n\text{-}C_4H_9)_4N][Cu(S_2C_2(CN)_2)_2]$.[41] Similarly, although the $(n\text{-}C_4H_9)_4N^+$ ion in $[(n\text{-}C_4H_9)_4N][Co(S_2C_2(CN)_2)_2]$[42] is ordered, even here three of the *n*-butyl chains adopt the *trans* conformation while the fourth takes up a *gauche* conformation.

These observations should result in some hesitation in using tetra-*n*-butylammonium salts in future crystallographic investigations.

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Crystal Structure and Absolute Configuration of (−)-Tetracarbonyl(fumaric acid)iron

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The molecular and crystal structure of (−)-tetracarbonyl(fumaric acid)iron ((−)-$Fe(CO)_4(CHCOOH)_2$) has been determined by X-ray diffraction methods. The unit cell of $P2_12_12$ symmetry (a = 6.10 (2) Å, b = 13.37 (4) Å, c = 19.20 (6) Å) contains six molecules of the $Fe(CO)_4(CHCOOH)_2$ formula. The measured and calculated densities are, respectively, 1.77 and 1.80 g cm^{-3}. A total of 610 nonzero intensities were collected photographically by Weissenberg equiinclination methods. The structure was determined by the Patterson method and refined by the least-squares method to a conventional R factor of 11.6%. A trigonal-bipyramidal coordination of the ligands around the central iron atom has been found. Two significantly different conformations are observed of the same molecule since only one of the three crystallographically independent molecules shows the C═C group of the coordinated fumaric acid lying on the equatorial plane. For two molecules, on the contrary, a significant deviation from the planarity is observed. The absolute configuration has been determined utilizing the anomalous diffraction of the Cu Kα radiation by the iron atom. According to the rule used by Cahn, Ingold, and Prelog the absolute configuration is *R,R*. Two different patterns of hydrogen bonding have been observed. Each molecule of type A is hydrogen bonded to four others of the same type. Molecules of type B and C, on the other hand, are hydrogen bonded according to the sequence. . . B–C–B–C. . . .

Introduction

Recent studies on olefin and transition metal complexes carried out in our laboratory have shown that when an olefinic compound without asymmetric substituents and with no symmetry plane normal to the plane of the double bond is π bonded to a coordinative center, pairs of enantiomorphic molecules are obtained.[1-8] The structures of some of these complexes containing Pt or Fe as the coordination center are under study in our laboratory. In this paper we report the results of a three-dimensional X-ray study on the (−)-$Fe(CO)_4(CHCOOH)_2$ complex.

Experimental Section

A sample of racemic tetracarbonyl(fumaric acid)iron, $Fe(CO)_4(CHCOOH)_2$, was prepared following the method described by

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