Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

A NOVEL METAL CLUSTER IN THE TETRAMETHYLAMMONIUM SALT OF THE DIOCTAHEDRAL TRIACONTACARBONYL DODECARHODATE DIANION, $[Rh_{12}(CO)_{30}]^{2-}$

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(Received June 9th, 1969)

SUMMARY

The crystal and molecular structure of the tetramethylammonium salt of the triacontacarbonyldodecarhodate dianion $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$ has been determined from three-dimensional X-Ray data collected by counter methods. The structure has been refined by least squares on 1800 F_o's down to an R factor of 0.05. This salt crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5) with the following cell parameters: $a=9.491(5)$ Å, $b=17.185(7)$ Å, $c=17.756(7)$ Å, $\beta=96°57'(15')$, $Z=2$.

The structure is composed of anionic and cationic layers. The anion is a centrosymmetric dimer of the $[Rh_6(CO)_{15}]^-$ unit. The catenation between the symmetry related sub-units takes place by a metal–metal bond and two CO groups bridged over it. The coordination pattern around the rhodium atoms is very similar to that found in the neutral molecule $Rh_6(CO)_{16}$ with the exception of the catenating Rh atoms which display nine-fold coordination.

The overall symmetry of the anion is D_{2h}. The metal cluster exhibits a range of Rh–Rh distances from 2.68 Å to 2.85 Å. The independent CO groups fall into 3 classes: 10 are linearly bonded, 4 are triply asymmetrically bridged on alternating octahedral faces and 1 is connecting the two octahedral sub-units through a symmetric double bridge.

INTRODUCTION

The syntheses and structures of the following carbonylic clusters of cobalt atoms, $Co_6(CO)_{16}$, $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ have been described recently[1-6]. On the basis of these results and the existence of $Rh_6(CO)_{16}$[7], the existence of corresponding anions was expected for rhodium.

Dichlorotetracarbonyldirhodium, $Rh_2(CO)_4Cl_2$, when treated with nucleophilic agents in presence of carbon monoxide, gives the analogues of the aforementioned cobalt clusters, *viz.* $Rh_6(CO)_{16}$ (ref. 8), $[Rh_6(CO)_{14}]^{4-}$ and probably $[Rh_6(CO)_{15}]^{2-}$ (ref. 9). The products have been characterized by chemical, spectroscopic and crystallographic examination. In addition to these, other products have been isolated which contain more complicated clusters, for example, $[Rh_{12}(CO)_{30}]^{2-}$ (ref. 10) and an anion containing seven metal atoms[11].

Questions about the molecular complexity, stereochemistry and the nature of the bonding in these new anions are of much interest, and so a detailed X-ray structural investigation of both species was undertaken. We shall discuss the structure of the heptarhodate anion in a separate publication, but we now describe the results obtained for tetramethylammonium dodecarhodate $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$.

EXPERIMENTAL

The salt $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$ (formula weight 2224) crystallizes in violet-black prisms. Preliminary precession photographs indicated a monoclinic symmetry. The systematic absences, $h0l$ with l odd and $0k0$ with k odd, indicate a space group $P2_1/c$ (N.14, C^5_{2h}). The unit cell parameters, determined from film data and refined on the PAILRED diffractometer with the ω-lag procedure outlined by Hornstra[12], have the following values at 20°: $a=9.491(5)$ Å, $b=17.185(7)$ Å, $c=17.756(7)$ Å, $\beta=96°57'(15')$, $V=2874.8$ Å^3. In these measurements the wavelength of MoKα radiation was taken as 0.70930 Å. The experimental crystal density, 2.50(3) $g \cdot cm^{-3}$ measured by a picnometer using toluene as picnometric liquid, is in agreement with the value of 2.56 $g \cdot cm^{-3}$ computed for two formula units per cell. The crystallographically independent unit is then $[N(CH_3)_4][Rh_6(CO)_{15}]$.

The intensity measurements were done on a PAILRED linear equi-inclination diffractometer. The incident beam was MoKα radiation as obtained from a monochromatizing single crystal[1,2] of silicon cut on [111]. The crystal used in the data collection was a thin parallelepiped with dimensions of $0.08 \times 0.11 \times 0.40$ mm; its direction of maximum elongation, coincident with the a axis of the cell; was oriented along the ω-axis of the instrument in order to minimize absorption effects. The integrated intensities of eight levels of the reciprocal lattice, from $0kl$ to $7kl$, were collected within a range $3° < \Upsilon < 52°$, the diffraction profiles were measured by the fixed counter-moving crystal method, at a scan rate of 0.5°/min; the scan range was 1° for the $0kl$–$3kl$ levels and 2° for the remaining $4kl$–$7kl$ levels. The backgrounds were measured for 20 seconds at the extreme points of the scan range. During the data collection the intensities of some zero-level reflections were tested periodically to see whether some crystal decay was taking place. However no significant variations of these standards were noticed. The final experimental set, after suppression of all the measurements having a relative statistical error $\sigma(I)/I > 0.25$, was one consisting of 1800 independent intensities. The absorption correction was computed by the Busing and Levy method[13]. Six crystal faces were carefully measured on a Stoe optical goniometer equipped with a Leitz screw micrometer. Because of the relatively low linear absorption coefficient ($\mu = 33.2$ cm^{-1}) a 216 points sampling (6^3) was adopted; the resulting transmission factors were in the range 0.65–0.72. The data were reduced to F_o values on an arbitrary scale by correcting them for Lorentz and polarization factors. The latter was evaluated by taking into account the partial polarisation of the monochromatized incident beam[14].

STRUCTURE SOLUTION AND REFINEMENT

The structure has been solved by applying the σ-two procedure of Karle and Hauptmann[15] to a set of 220 E values greater than 1.8. The detailed procedure used here has been reported elsewhere[6]. In the present case only one of the 16 signed E-sets obtained after convergence of the signing procedure appeared to be promising on the basis of the number of cycles necessary to get to convergence. The corresponding Fourier map did show quite clearly the positions of the six independent metal atoms. A structure factor computation with the contribution of these atoms only gave an R factor of 0.36. A difference synthesis did then reveal all the light atoms of the structure.

The refinement was done by least squares in the block-diagonal approximation because of the limited computing facilities in the author's laboratory. The blocks were 9×9 for the heavy atoms treated anisotropically and 4×4 for the light ones, treated isotropically. The scale factor was correlated with the mean overall temperature factor of the structure in a 2×2 block[16]. The minimized function was $\Sigma w(F_o - k\cdot|F_c|)^2$.

The atomic scattering factors used in the least-squares as well as in the structure factors computations, were chosen as follows: for rhodium the T.F.D. statistical model curves[17] corrected for the real part of the anomalous dispersion, for oxygen, nitrogen and carbon the curves from the self-consistent variational method[18]. The weights w were the reciprocal of the F_o's variance, this variance was computed from the variance of the corresponding F_o^2 assumed to be[19] $V(F_o^2) = V_{cs}(F_o^2) + (A\cdot F_o^2)^2$, where $V_{cs}(F_o^2)$ is the counting statistical variance and A is a parameter chosen in such a way as to render the distribution of the mean weighted quadratic error approximately constant as a function of $\sin\theta/\lambda$ and of F_o. In this case a value of $A = 0.03$ was satisfactory.

The refinement has converged to the following reliability indices:

$$R = \frac{\Sigma(|F_o - k\cdot|F_c||)}{\Sigma F_o} = 0.050 \text{ and } R\cdot w = \{\Sigma w(F_o - k\cdot|F_c|)^2/\Sigma w\cdot F_o^2\}^{\frac{1}{2}} = 0.070$$

A final difference Fourier has not shown peaks higher than 1 $e^-/\text{Å}^3$. The $|F_c|$ and the F_o/k values obtained after convergence are listed in Table 1. The positional and thermal anisotropical parameters of the six rhodium atoms are collected in Table 2; the positional and thermal isotropic parameters of the C, N and O atoms are collected in Table 3. The e.s.d. of each parameter reported in these Tables is derived from the appropriate diagonal element of the L.S. blocks.

DESCRIPTION OF THE STRUCTURE

One of the metal atoms of the crystallographically independent part of the anion at 1.41 Å from a center of symmetry (a type position in space group $P2_1/c$). This fact implies the existence of a bond twice as long between two corresponding metal atoms of two units $[Rh_6(CO)_{15}]^-$ related by inversion. The structure of the anion lies at 1.41 Å from a center of symmetry (a type position in space group $P2_1/c$). through a metal–metal bond. Two CO groups are found in such a position as to form bridges on the two inversion-related metal atoms. Fig. 1 is a perspective view of the anion, a detailed discussion of it is given in the next section of this paper.

The main axis of the anion is almost coincident with b, the unique axis of the cell. Further, atoms Rh_1, Rh_2, Rh_3 and Rh_4 are approximately coplanar with the (100) plane. The crystal packing is formed by anionic layers separated by a distance equal to 9.42 Å $= a\cdot\sin\beta$. The cavities of this packing are occupied by the cations

(*continued* p. 412)

TABLE 1

OBSERVED AND COMPUTED STRUCTURE FACTOR MODULI IN ELECTRON UNITS FOR $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$

H	L	FO	/FC/
K = 0			
4	2	46	49
5	2	215	222
6	2	119	136
7	2	94	90
0	4	167	157
1	4	142	136
2	4	94	82
2	-4	114	109
3	4	206	189
4	4	112	99
4	-4	249	243
5	4	139	139
6	4	116	105
7	4	45	38
0	6	104	109
1	6	280	254
1	-6	61	56
2	6	84	87
2	-6	190	171
3	-6	94	95
4	6	259	255
4	-6	44	42
5	6	309	418
6	6	272	277
7	6	108	117
7	-6	89	82
0	8	319	319
1	8	305	287
1	-8	183	176
2	8	179	176
3	8	55	50
3	-8	104	101
4	8	195	186
4	-8	132	131
5	8	235	245
5	-8	98	106
6	8	183	182
7	8	87	95
0	10	216	214
1	10	122	126
1	-10	85	86
2	10	88	82
3	-10	53	62
4	-10	119	129
5	10	75	76
5	-10	123	114
6	10	66	66
1	12	45	48
6	12	63	60
1	16	57	51
6	-16	69	70
0	18	96	63
1	18	89	86
3	-18	71	66
4	-18	81	76
3	-20	72	65
4	-20	72	96
1	-22	94	94
K = 1			
1	3	32	40
2	3	101	98
3	3	72	71
0	4	76	70
2	4	56	53
2	-4	109	107
3	4	98	95
3	-4	47	53
4	-4	123	126
5	4	56	48
1	5	179	172
1	-5	64	63
2	5	105	96
2	-5	32	31
4	5	99	99
5	5	118	120
5	-5	49	51
6	5	91	89
0	6	106	106
1	-15	82	85
2	15	69	71
2	-15	102	98
3	15	72	66
3	-15	76	77
4	-15	58	59
5	-15	67	57
0	16	66	71
1	16	140	144
3	16	99	76
2	-16	80	95
5	16	105	102
6	16	118	135
6	-16	89	103
0	17	53	53
1	-17	47	50
2	-17	57	50
3	-17	65	61
0	18	90	93
1	18	120	113
2	18	95	79
3	-18	65	65
4	-18	61	74
6	18	71	59
3	-20	63	52
K = 3			
3	2	305	311
1	3	29	24
1	-3	37	42
2	3	119	110
2	-3	62	63
3	3	99	93
7	3	50	55
1	4	69	65
2	4	363	353
2	-4	417	333
3	4	360	359
3	-4	109	107
4	4	115	110
4	-4	55	63
7	4	95	104
7	-4	44	54
1	-5	104	105
2	5	143	134
2	-5	293	292
3	5	199	193
3	-5	200	195
7	5	57	53
7	-5	86	93
0	6	59	49
1	-6	66	56
2	6	129	121
2	-6	344	349
3	6	168	175
3	-6	276	279
5	6	123	124
6	6	128	129
6	-6	102	104
7	-6	176	190
0	7	65	53
1	-7	129	123
2	-7	215	212
3	7	98	93
3	-7	140	147
4	-7	47	47
5	7	56	61
6	-7	108	111
7	-7	149	133
0	8	62	62
1	8	125	125
1	-8	72	73
2	-8	127	127
3	-8	96	99
5	8	116	113
6	8	60	57
6	-8	100	103
7	-8	136	134
0	9	143	142
1	9	134	129
1	-9	52	64
2	9	45	44
1	4	78	69
1	-4	176	174
2	-4	323	320
3	4	114	102
3	-4	44	46
5	-4	54	55
7	-4	55	60
1	-5	196	194
2	5	273	264
2	-5	357	347
3	5	327	320
3	-5	305	306
4	5	107	100
4	-5	63	70
5	5	66	66
7	-5	153	154
0	6	111	97
1	6	40	47
2	-6	229	235
3	-6	155	160
5	6	107	110
6	6	93	93
6	-6	67	73
7	-6	126	127
0	7	87	83
1	7	157	143
1	-7	41	36
3	-7	144	135
3	7	49	51
3	-7	81	81
4	7	55	40
5	7	131	129
6	7	102	103
6	-7	78	87
7	-7	122	121
0	8	171	163
1	8	203	204
1	-8	63	77
2	8	45	49
4	8	66	64
4	-8	90	86
5	8	136	131
6	8	66	67
7	-8	98	100
0	9	161	155
1	9	120	124
1	-9	67	64
2	9	96	96
3	-9	86	78
4	-9	133	134
5	9	56	40
5	-9	102	108
0	10	139	143
1	10	149	153
1	-10	73	74
3	10	83	87
4	10	65	56
4	-10	170	172
5	-10	94	110
0	11	40	36
3	-11	53	51
1	-12	106	108
2	12	99	103
2	-12	115	103
3	12	192	194
4	12	96	101
4	-12	55	63
5	-12	72	63
7	-13	59	40
0	14	70	73
1	-14	154	162
2	14	80	82
2	-14	170	178
3	14	113	114
3	-14	84	85
6	-14	90	106
7	-14	85	78
0	15	74	65
1	15	59	57
1	-15	71	78
2	15	70	72
2	-15	67	67
5	-15	74	65
5	-9	77	73
6	-9	100	98
7	9	93	93
7	-9	169	170
0	11	54	48
1	-11	80	73
2	11	142	143
2	-11	160	167
3	11	266	267
4	11	171	174
5	-11	125	124
6	11	57	52
7	11	132	141
7	-11	77	72
0	13	132	132
1	13	101	99
1	-13	260	265
2	13	190	194
2	-13	284	282
3	13	256	269
3	-13	105	108
4	13	201	196
5	13	72	72
6	-13	93	96
7	-13	107	95
2	14	54	45
1	-15	193	186
2	-15	205	214
3	15	92	98
3	-15	101	103
5	-15	93	91
6	15	70	73
6	-15	153	153
7	-15	152	149
0	16	67	48
1	16	64	61
1	17	117	118
2	17	79	67
2	-17	55	50
4	-17	56	47
6	17	66	60
6	-17	96	88
0	18	63	39
3	-18	63	50
1	19	70	69
4	-19	73	77
K = 5			
2	0	46	47
3	0	113	111
4	0	79	78
6	0	41	53
7	0	42	36
0	1	129	127
1	1	58	55
1	-1	164	155
2	1	361	362
2	-1	179	175
3	1	412	433
3	-1	138	129
4	1	142	144
4	-1	91	77
5	-1	140	149
7	1	303	313
7	-1	182	186
0	2	45	44
1	2	144	144
1	-2	106	108
2	2	71	63
2	-2	118	117
3	2	60	63
3	-2	80	91
4	2	77	76
4	-2	56	55
1	3	185	185
1	-3	287	299
2	3	532	528
2	-3	490	496
3	3	545	552
3	-3	265	271
4	3	312	320
5	3	103	110
3	4	139	119
3	-4	127	141
4	-4	82	82
5	-4	45	46
6	-4	105	96
1	5	66	61
1	-5	186	186
2	5	192	195
2	-5	267	276
3	5	212	213
3	-5	238	243
4	5	94	92
4	-5	73	74
5	5	61	51
6	-5	127	123
7	-5	144	156
1	-6	78	88
2	-6	104	104
3	-6	89	94
4	-6	57	54
5	-6	57	62
6	-6	132	141
7	-6	88	98
0	7	136	140
1	7	73	63
1	-7	117	114
2	-7	237	247
3	7	109	100
3	-7	206	208
5	7	119	120
6	7	94	97
6	-7	147	145
7	-7	187	199
0	8	82	83
2	-8	47	50
3	8	76	83
4	8	69	66
7	8	69	67
7	-8	73	71
0	9	196	205
1	9	195	190
2	-9	76	79
3	9	86	85
4	-9	140	143
5	-9	130	129
7	9	57	57
7	-9	125	129
0	10	120	121
1	10	112	116
1	-10	135	141
2	10	145	151
2	-10	117	118
3	10	194	197
3	-10	55	61
4	10	148	155
5	10	89	97
6	10	95	91
7	10	93	96
7	-10	49	37
0	11	81	77
1	11	81	72
1	-11	50	58
2	11	95	97
2	-11	118	128
3	11	194	198
4	11	130	118
4	-11	171	181
5	-11	149	152
7	11	90	95
7	-11	57	50
0	12	168	167
1	12	135	130
1	-12	198	199
2	12	133	136
2	-12	148	159
3	12	120	124
3	-12	139	147
4	12	96	119
4	-12	114	119
5	12	76	76
5	-12	118	125
6	-12	107	107
7	-12	81	79
2	5	118	111
2	-5	155	156
3	5	156	162
3	-5	96	105
5	5	151	156
5	-5	122	130
6	5	105	106
0	6	72	70
2	6	54	55
2	-6	62	61
3	-6	85	91
5	6	73	90
5	-6	77	75
0	7	165	163
1	7	172	171
4	7	110	135
4	-7	51	58
5	7	154	159
6	7	133	135
7	7	51	54
0	8	198	203
1	8	185	196
1	-8	71	69
2	8	57	53
2	-8	61	60
3	8	53	44
4	8	87	80
4	-8	65	61
5	8	136	145
5	-8	91	94
6	8	124	126
7	-8	59	60
0	9	224	229
1	9	222	230
1	-9	105	105
2	9	122	116
3	9	67	84
3	-9	51	56
4	9	109	117
4	-9	107	117
5	9	120	128
5	-9	82	97
6	9	124	124
7	9	63	62
0	10	192	191
1	10	174	175
1	-10	107	101
2	10	64	70
2	-10	55	50
3	-10	124	122
4	10	60	50
4	-10	151	147
5	10	79	78
5	-10	110	112
6	10	59	61
6	-10	49	41
0	11	169	167
1	11	139	146
1	-11	119	119
2	11	88	90
2	-11	98	106
3	-11	77	80
4	-11	99	107
5	11	81	72
5	-11	97	90
6	-11	67	64
7	-11	59	43
2	-12	63	58
4	12	64	53
4	-12	75	83
0	13	90	85
1	13	70	77
1	-13	102	104
2	13	61	75
2	-13	91	103
3	13	62	53
4	-13	65	73
5	-13	99	89
6	-13	89	89
7	-13	60	68
1	-14	99	93
2	-14	101	114
3	14	73	62
3	-8	110	105
4	8	84	99
4	-8	131	137
5	8	126	122
5	-8	95	109
6	8	109	109
7	-8	44	26
0	9	160	169
1	9	160	165
1	-9	66	71
2	9	94	91
3	-9	92	99
4	-9	113	134
5	-9	139	134
3	10	64	40
4	-10	80	91
0	11	75	91
1	11	82	95
3	11	87	88
3	-11	87	92
4	-11	143	151
5	-11	145	143
0	12	59	65
1	-12	51	50
2	-12	52	53
6	-12	61	33
1	-13	54	55
2	-13	56	63
4	-13	76	97
5	-13	77	75
1	15	60	53
2	-15	81	91
0	17	61	59
6	17	69	59
1	18	67	62
2	19	63	65
K = 9			
1	0	56	56
0	1	163	163
1	1	133	132
1	-1	125	123
4	1	56	52
4	-1	69	71
5	1	126	113
5	-1	117	121
6	-1	69	71
0	2	148	145
1	2	133	143
1	-2	142	143
2	2	46	36
3	-2	65	66
4	2	71	72
4	-2	87	91
5	2	86	84
5	-2	167	179
6	-2	106	113
0	3	113	117
1	3	67	61
1	-3	47	51
2	3	69	56
3	3	45	42
4	-3	117	115
5	-3	117	117
6	-3	79	67
0	4	104	105
1	-4	55	65
2	4	57	60
4	-4	137	139
5	-4	107	113
6	-4	88	74
7	-4	63	37
1	5	56	59
2	5	75	77
2	-5	64	68
3	5	63	67
3	-5	70	79
4	-5	45	44
0	6	104	103
1	6	137	132
2	-6	65	59
3	-6	52	41
5	1	83	82
0	2	300	303
1	2	188	188
1	-2	192	197
2	2	50	49
3	2	122	127
4	-2	240	241
5	2	117	121
5	-2	277	280
6	-2	144	148
7	2	90	99
7	-2	49	46
0	3	104	104
1	-3	103	92
2	-3	95	89
5	-3	71	61
6	3	50	49
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2	-3	101	97
3	3	66	64
1	-4	63	69
2	4	97	87
2	-4	124	127
3	4	65	62
3	-4	73	71
6	4	54	41
7	-4	54	55
1	5	53	51
4	5	57	55
5	5	80	78
6	5	76	72
7	-5	58	47
0	6	73	79
1	6	74	80
2	-6	113	114
5	6	89	93
6	6	81	86
7	-6	104	111
0	7	149	152
1	7	151	143
1	-7	102	112
2	7	118	113
2	-7	118	118
3	7	80	99
3	-7	135	137
4	7	79	93
4	-7	116	112
5	7	87	97
5	-7	64	72
6	7	71	61
0	8	167	173
1	8	166	170
2	-8	58	60
4	-8	94	93
5	8	110	110
5	-8	71	72
6	8	87	95
7	-8	125	126
0	9	91	93
1	9	93	97
1	-9	57	61
2	-9	100	107
3	-9	133	135
4	-9	145	140
5	-9	113	116
6	-9	111	102
7	-9	107	107
0	10	120	132
1	10	113	117
3	10	90	86
3	-10	63	58
4	-10	136	145
5	-10	132	135
3	-11	55	54
4	-11	86	83
6	-11	40	43
0	12	48	46
1	12	52	41
1	-12	78	70
2	-12	91	93
3	12	125	139
4	12	91	100
4	-12	96	96
5	-12	79	81
2	13	78	88
5	13	91	84
6	13	71	88
1	-14	116	120
2	-14	155	158
3	14	113	106
6	-14	73	66
7	-14	65	72
0	15	92	92
1	15	109	113
1	-15	101	109
2	15	122	127
2	-15	116	117
3	15	115	116
3	-15	97	100
4	-15	65	64
6	15	78	72
7	15	66	64
1	-16	63	60
2	-16	88	92
6	-16	90	82
7	-16	87	79
0	17	65	70
1	17	69	70
1	-17	79	92
2	17	76	75
2	-9	106	103
3	9	62	65
3	-9	81	93
6	-9	69	67
7	-9	100	97
2	-10	49	46
6	-10	65	56
7	-10	67	71
2	11	56	50
2	-11	64	65
3	11	84	92
1	-13	85	86
2	13	62	58
2	-13	90	92
3	13	86	93
0	16	61	70
1	16	77	77
2	16	62	64
4	-16	71	58
0	17	58	52
K = 13			
4	0	75	79
5	0	70	59
1	1	77	76
1	-1	90	80
2	1	213	214
2	-1	163	164
3	1	211	216
3	-1	152	156
4	1	100	100
6	1	99	99
7	1	171	178
7	-1	108	112
0	2	74	83
1	2	63	62
1	-2	97	104
2	2	107	111
2	-2	118	115
3	2	107	114
4	2	65	76
5	2	63	53
0	3	104	104
1	3	139	145
1	-3	157	162
2	3	260	266
2	-3	252	261
3	3	249	262
3	-3	172	181
4	3	133	138
5	3	69	67
6	3	89	91
6	-3	65	61
7	3	147	156
7	-3	106	105
0	4	47	37
1	-4	103	105
2	-4	165	174
3	-4	96	106
6	4	59	49
6	-4	99	91
0	5	52	57
1	5	79	79
1	-5	164	164
2	5	143	139
2	-5	220	228
3	5	140	150
3	-5	140	152
4	5	91	86
5	-5	92	90
6	-5	124	143
7	-5	144	148
1	6	66	73
2	-6	80	77
3	-6	60	47
7	-6	110	113
2	-7	77	83
3	7	66	58
4	7	62	48
7	-7	83	80
0	8	57	64
1	8	76	77
2	-8	46	36
7	-8	70	75
3	9	75	87
4	9	83	85
4	-9	56	45
1	-10	52	52
3	10	88	91
4	10	84	77
4	-10	55	52
0	11	82	84
4	0	117	114
5	0	77	83
0	1	140	143
1	1	57	62
1	-1	67	58
2	1	64	65
2	-1	63	68
3	1	76	83
4	-1	71	65
5	1	59	56
5	-1	100	110
7	1	64	78
7	-1	54	54
0	2	137	140
1	2	89	87
1	-2	162	169
2	2	86	99
2	-2	109	119
3	2	121	118
3	-2	68	70
4	2	107	103
0	3	69	74
2	3	99	107
2	-3	110	110
3	3	125	120
3	-3	68	64
4	-3	62	68
5	-3	89	99
7	3	68	69
7	-3	66	48
0	4	72	72
1	-4	103	106
2	-4	95	100
3	-4	73	82
4	-4	73	73
5	4	56	25
5	-4	80	75
6	-4	85	82
7	-4	71	69
2	-5	121	121
3	5	98	90
3	-5	65	72
5	5	83	71
6	5	60	58
7	-5	65	70
1	6	73	66
2	6	56	46
0	7	89	94
2	-7	69	64
5	7	90	88
6	7	74	65
0	9	84	87
1	9	59	60
K = 16			
0	0	88	86
0	5	66	69
4	5	53	25
5	5	85	66
0	6	56	59
2	6	68	70
5	6	61	66
6	6	64	50
0	7	92	92
1	7	81	74
4	-7	63	61
5	7	78	69
5	-7	68	62
0	8	47	32
4	-8	76	72
0	9	94	97
1	9	83	94
4	-9	85	93
5	-9	78	83
0	10	82	80
1	-10	69	72
3	10	78	81
4	10	80	91
1	11	72	69
4	-11	97	97
0	12	107	114
1	12	82	84
1	-12	122	125
2	-12	97	100
3	-12	87	90
4	-12	77	82
5	-12	96	90
3	13	66	47
1	-14	59	47
5	-14	83	78
K = 17			

(*continued* p. 410)

TABLE 1 (*continued*)

H	L	FO	/FC/
4	0	66	70
0	1	174	172
1	1	111	113
1	-1	106	106
4	1	78	68
4	-1	97	93
5	1	106	112
5	-1	122	123
6	1	66	65
6	-1	76	72
0	2	114	116
1	2	78	90
1	-2	115	124
2	2	64	69
3	2	98	95
4	2	91	93
4	-2	64	59
0	3	141	143
1	3	79	86
1	-3	94	96
4	-3	107	100
5	3	95	95
5	-3	116	125
6	3	69	65
6	-3	70	72
0	4	72	78
1	-4	94	99
2	-4	65	65
3	-4	72	64
4	-4	82	86
5	-4	102	96
6	-4	77	96
0	5	92	90
4	-5	74	75
5	-5	105	98
5	6	76	28
0	7	69	65
5	7	90	74
0	8	79	72
4	8	66	60
0	9	69	67
0	10	79	83
1	10	89	81
3	-10	57	37
4	10	74	60
5	10	72	66
0	11	73	70
1	11	64	59
0	14	48	30
K = 18			
0	0	142	156
1	0	101	107
3	0	64	56
4	0	99	105
5	0	126	117
6	0	67	71
4	1	82	72
0	2	126	128
1	2	88	87
1	-2	72	70
4	2	63	54
4	-2	112	112
5	2	96	96
5	-2	120	120
6	-2	64	64
2	-3	67	59
0	4	91	96
4	-4	66	67
5	4	102	104
6	4	83	81
0	5	62	71
1	5	91	92
2	5	63	65
5	5	81	75
0	6	111	114
1	6	128	127
1	-6	55	57
4	-6	91	83
5	6	94	103
7	6	64	45
0	7	81	85
1	7	92	93
0	8	100	103
1	8	92	105
1	-8	58	64
2	8	70	66
3	-8	85	89
4	-8	106	103
5	8	93	56
0	9	56	50
1	9	61	55
4	-9	91	76
K = 19			
0	2	59	49
0	3	49	44
7	5	67	41
0	7	56	54
1	7	63	70
1	-7	69	72
2	-7	96	99
3	7	70	66
3	-7	83	92
4	-7	69	65
2	-9	75	72
3	-9	86	90
0	10	68	52
0	15	66	66
K = 20			
2	0	87	88
3	0	77	77
1	-1	66	51
3	1	74	70
2	2	79	78
2	-2	80	87
3	2	91	89
3	-2	73	70
1	-3	66	67
2	-3	65	58
2	-4	84	92
2	5	70	83
6	5	74	66
0	7	67	59
1	7	75	80
K = 21			
0	3	53	45
1	-3	65	62
2	-3	66	65
K = 22			
2	0	75	77
3	0	73	71
0	3	53	38
K = 23			
0	2	51	40

TABLE 2

FINAL ATOMIC COORDINATES FOR ANISOTROPICALLY REFINED ATOMS IN $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$

All values × 10^4; anisotropic temperature factors are in the form: $\exp[-(h^2\cdot\beta_{11}+k^2\cdot\beta_{22}+l^2\cdot\beta_{33}+h\cdot k\cdot\beta_{12}+h\cdot l\cdot\beta_{13}+k\cdot l\cdot\beta_{23})]$.

Atoms	x/a	y/b	z/c	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Rh1	19 (2)	815 (1)	−68 (1)	56 (2)	0 (2)	4 (1)	14 (0)	−1 (0)	16 (0)
Rh2	384 (3)	2131 (1)	909 (1)	99 (3)	−11 (2)	11 (2)	22 (0)	−9 (1)	19 (0)
Rh3	41 (2)	3132 (1)	−315 (1)	84 (3)	0 (2)	8 (2)	16 (0)	−2 (1)	28 (0)
Rh4	−323 (2)	1886 (1)	−1298 (1)	79 (2)	−1 (2)	0 (2)	19 (0)	1 (1)	18 (0)
Rh5	−1971 (2)	2043 (1)	−78 (1)	65 (2)	10 (2)	18 (2)	20 (0)	2 (1)	27 (0)
Rh6	2038 (2)	1982 (1)	−301 (1)	64 (2)	−6 (2)	9 (2)	19 (0)	−4 (1)	21 (0)

TABLE 3

FINAL ATOMIC COORDINATES FOR ISOTROPICALLY REFINED ATOMS IN $[N(CH_3)_4]_2[Rh_{12}(CO)_{30}]$

All values × 10^4

Atoms	x/a	y/b	z/c	B(Å²)	Atoms	x/a	y/b	z/c	B(Å²)
C 11	−881 (27)	73 (11)	588 (12)	2.3 (4)	C 61	3159 (37)	1362 (17)	−829 (16)	4.6 (6)
O 11	−1658 (21)	120 (9)	1052 (9)	3.7 (3)	O 61	3959 (29)	1061 (13)	−1188 (13)	6.7 (5)
C 21	−248 (33)	1565 (14)	1731 (14)	3.5 (5)	C 62	3536 (26)	2568 (11)	239 (11)	1.8 (3)
O 21	−585 (26)	1225 (11)	2222 (11)	5.3 (4)	O 62	4359 (27)	2956 (11)	493 (12)	5.8 (5)
C 22	1803 (34)	2660 (16)	1524 (15)	4.1 (6)	C126	1887 (27)	1092 (11)	633 (12)	2.1 (4)
O 22	2744 (30)	2917 (13)	1947 (13)	6.6 (5)	O126	2741 (22)	850 (10)	1068 (10)	4.3 (4)
C 31	1201 (39)	3901 (18)	68 (17)	5.1 (7)	C145	−1759 (28)	980 (12)	−789 (12)	2.4 (4)
O 31	2064 (31)	4371 (14)	337 (14)	7.5 (6)	O145	−2739 (21)	676 (9)	−1158 (9)	3.8 (3)
C 32	−1139 (33)	3801 (14)	−903 (15)	3.6 (5)	C235	−1170 (35)	2979 (15)	665 (15)	3.9 (5)
O 32	−1924 (27)	4197 (12)	−1310 (12)	6.3 (5)	O235	−1751 (25)	3467 (11)	1035 (11)	4.8 (4)
C 41	401 (31)	1194 (13)	−1974 (14)	3.1 (5)	C346	1287 (32)	2723 (14)	−1221 (14)	3.2 (5)
O 41	699 (26)	817 (11)	−2449 (11)	5.5 (4)	O346	1846 (22)	3091 (10)	−1669 (10)	3.9 (3)
C 42	−1819 (32)	2260 (13)	−2021 (14)	3.0 (4)	N	4106 (28)	50 (12)	3090 (12)	3.8 (4)
O 42	−2725 (29)	2485 (13)	−2462 (13)	6.6 (5)	CN1	2489 (39)	48 (16)	2883 (17)	5.1 (6)
C 51	−3146 (33)	1587 (14)	583 (14)	3.5 (5)	CN2	4487 (45)	257 (20)	3979 (19)	6.4 (8)
O 51	−3871 (29)	1348 (13)	1011 (13)	6.6 (5)	CN3	4722 (49)	667 (21)	2613 (22)	7.5 (9)
C 52	−3459 (38)	2486 (17)	−713 (17)	6.9 (6)	CN4	4655 (49)	−752 (21)	2977 (21)	7.3 (9)
O 52	−4356 (28)	2769 (12)	−1064 (12)	4.2 (5)					

$[N(CH_3)_4]^+$ which are found to occur in staggered planes interleaved with the anionic planes (the x coordinates of the cations are 0.41 and 0.59).

The cations do not depart significantly from their expected tetrahedral shape. The mean value of the N–C bond lengths in this structure is 1.54(3) Å, as compared with the commonly accepted[20] value of 1.48 Å. An extensive computation of all possible non-bonding interactions has not revealed significant departures from the expected contacts.

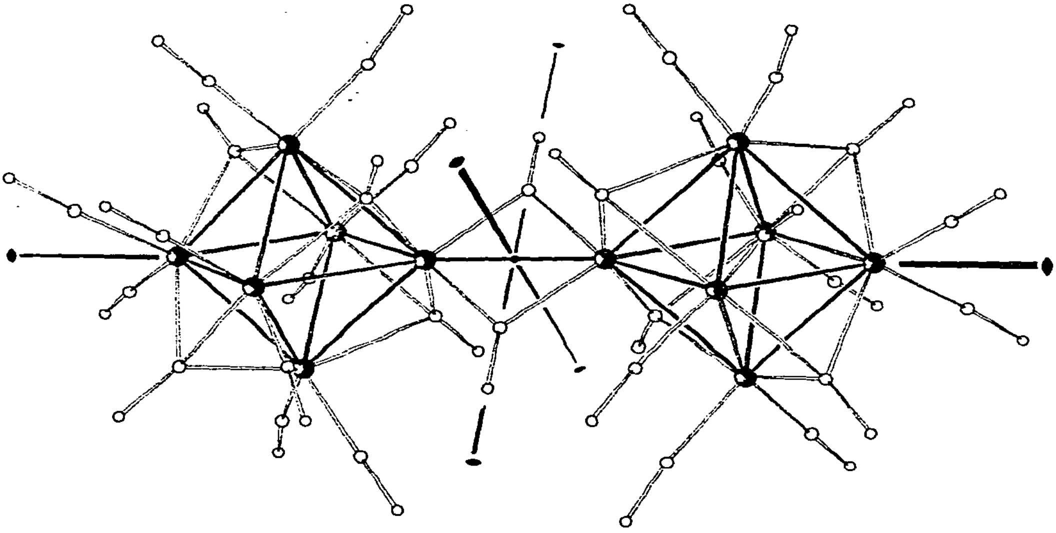

Fig. 1. Perspective view of the anion $[Rh_{12}(CO)_{30}]^{2-}$. The orientation of three mutually perpendicular diads of point group D_{2h} is also shown.

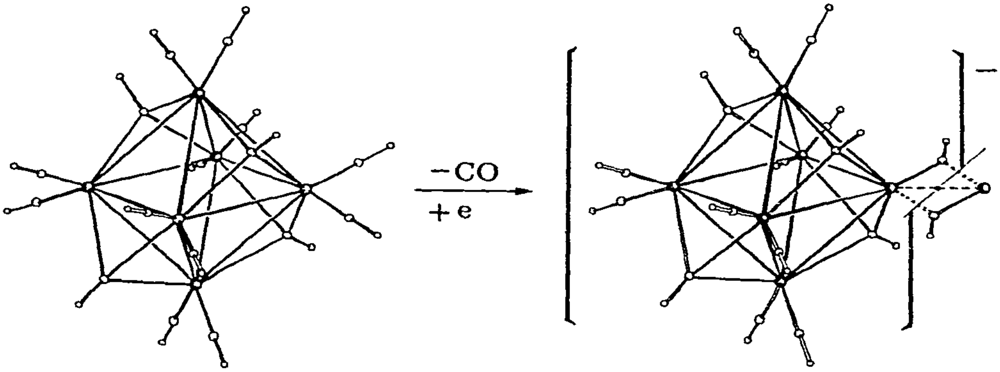

Fig. 2. Relationship between $Rh_6(CO)_{16}$ and $[Rh_{12}(CO)_{30}]^{2-}$.

THE TRIACONTACARBONYL DODECARHODATE ANION

The sub-unit $[Rh_6(CO)_{15}]^-$ which represents the crystallographic independent part of the anion may be thought of as derived from the neutral species $Rh_6(CO)_{16}$ by subtracting a carbonyl group and adding one electron. This hypothetical reaction

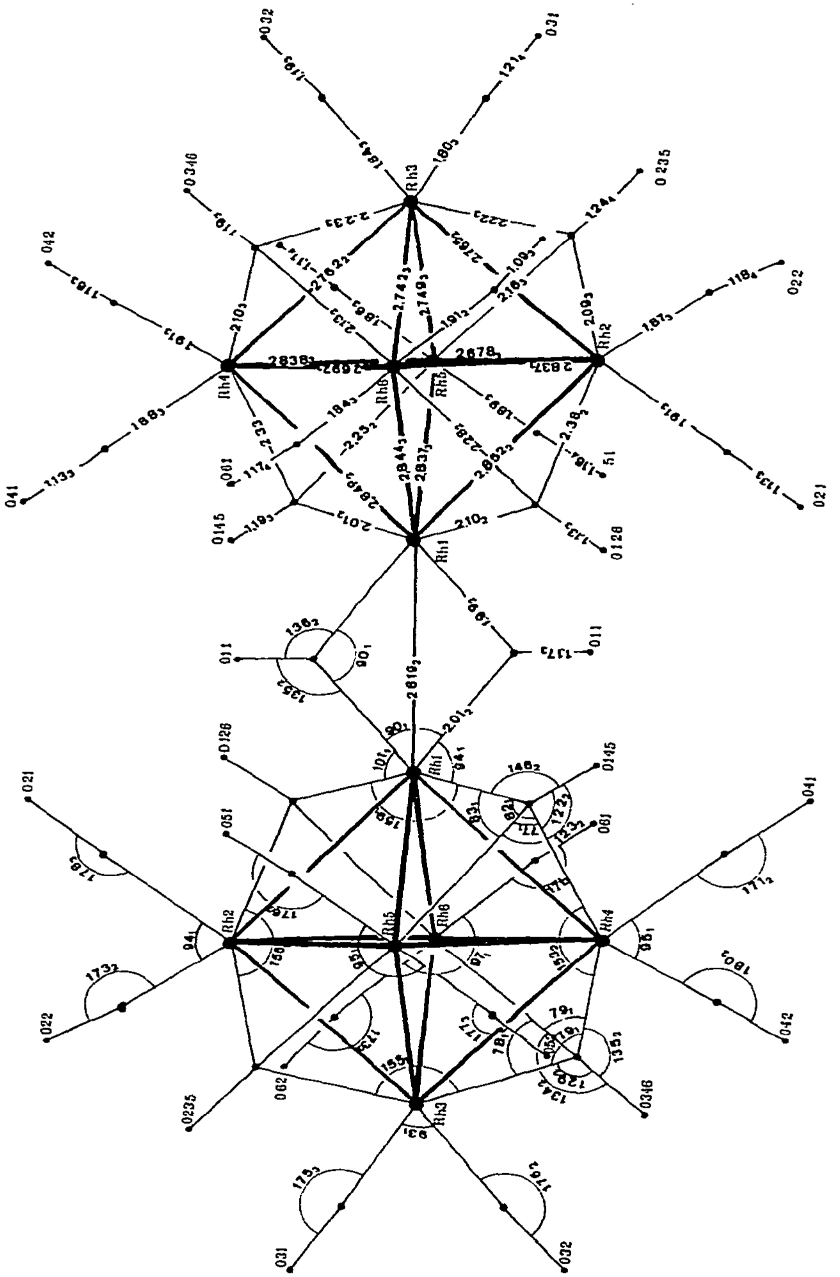

Fig. 3. Bond lengths and angles with their e.s.d.'s in $[Rh_{12}(CO)_{30}]^{2-}$.

is represented in Fig. 2 where the stereochemical relationship among the two species is shown.

Bond distances and angles of the anion, together with e.s.d.'s computed from the corresponding values of the least squares refinement, are reported in Fig. 3, where the atomic labelling which will be used in the following discussion is given.

In the sub-unit, the five metal atoms, which are not involved in the catenation exhibit exactly the same coordination pattern (referred as "tetragonal antiprismatic" by Dahl[7]), as in the neutral parent species. The catenating metal atom does not greatly depart form this scheme but is, in fact, nine-coordinated. The T_d symmetry of $Rh_6(CO)_{16}$ is destroyed, in the present anion. The presence of two catenated sub-units, obviously, does not admit any of the C_3 and S_4 axes of the T_d group. More than that, the Rh–Rh distances appear to be widely scattered. However their mean value 2.77 Å compares well with the corresponding value[7] of 2.78 Å in the neutral cluster.

The deformations of the octahedral moiety may be summarized in this way: (*i*) the four atoms Rh_2, Rh_4, Rh_5 and Rh_6 defining the "equatorial" plane, occupy the corners of a rectangle with dimension 2.68(1) Å × 2.84(1) Å; (*ii*) the distances of these atoms from the catenating Rh are all equivalent [2.84(1) Å] and so do the corresponding distances from the "apical" Rh_3[2.75(1) Å]. The difference among the two last groups of distances implies a lower bond order for the first one and is a consequence of the higher coordination number around it. In this range of distances the separation of 2.82(1) Å between the two catenated Rh_1 atoms appear not unusual. We may note also that none of the present Rh–Rh interactions is a novelty; these distances can be compared with the following values: 2.62 Å in $Rh_3(\pi\text{-}Cp)_3(CO)_3$[21], 2.68 Å in $Rh_2(\pi\text{-}Cp)_2(CO)_3$[22], 2.69 Å in Rh metal[20], 2.72 Å in $Rh_3(C_{20}H_{21})$[23], 2.73 Å in $Rh_4(CO)_{12}$[24], 2.85 Å in $Ru_3(CO)_{12}$[25], 2.85–2.95 Å in $Ru_6C(CO)_{14}$(Arene)[26].

The deformations described above for the metal octahedra are in agreement with a point group D_{2h}. Fig. 1 shows three mutually perpendicular diads intersecting at the center of symmetry of the anion. The spatial distribution as well as the bonding distances and angles of all the carbonyl groups follow the same symmetry. So, the eight CO groups linearly bonded to the equatorial Rh_2, Rh_4, Rh_5 and Rh_6 exhibit a narrow range of Rh–C and C–O distances [mean values 1.88(1) Å and 1.14 (1) Å respectively], whereas the corresponding distances for the groups bonded to the "apical" Rh_3 exhibit a different range [1.82(2) Å and 1.20(2) Å]. A comparison of these distances suggest a more pronounced metal-to-carbon π-bonding in the apical Rh–C–O interactions.

The face bridging groups show a departure from the threefold symmetry they display in $Rh_6(CO)_{16}$. Here again the spread in metal–carbon and carbon–oxygen distances and also the pattern of the angular distortion is in agreement with the D_{2h} group. The situation can be described as follows: the inner groups, bridging on the catenating and equatorial atoms, display one shorter [2.05(3) Å] and two longer [2.31(3) Å] values; the reverse is true for the outer groups bridging on the apical and equatorial atoms, one distance being longer [2.22(2) Å] and two shorter [2.12(2) Å]. The mean C–O distance for all these groups is 1.19(3) Å.

The group bridged on the Rh–Rh bond between the two sub-units lies along one of the diads within the standard deviations of its bonding parameters and has the following bond distances: Rh–C 2.00(2) Å and C–O 1.17(3) Å.

The spread of the Rh–Rh and Rh–C bond lengths, which accompanies the decrease of symmetry, indicates an overall decrease of the electron delocalisation within the $[Rh_6(CO)_{15}]^-$ moiety of the cluster; stated in a different way, the connection of the two octahedral sub-units destroyes the degeneracy of sets of molecular orbitals in an analogous way as the conjugation between aromatic rings does with respect to an aromatic π-system.

ACKNOWLEDGEMENTS

The Authors wish to thank V. Scatturin and P. Chini (the latter who also has kindly supplied the crystal samples) for their interest and a number of discussions. The financial support of the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged.

REFERENCES

1 P. CHINI, *Chem. Commun.*, (1967) 440.
2 V. ALBANO, P. CHINI AND V. SCATTURIN, *Chem. Commun.*, (1968) 163.
3 P. CHINI AND V. ALBANO, *J. Organometal. Chem.*, 15 (1968) 433.
4 V. ALBANO, P. CHINI AND V. SCATTURIN, *J. Organometal. Chem.*, 15 (1968) 423.
5 P. CHINI, V. ALBANO AND S. MARTINENGO, *J. Organometal. Chem.*, 16 (1969) 471.
6 V. ALBANO, P. L. BELLON, P. CHINI AND V. SCATTURIN, *J. Organometal. Chem.*, 16 (1969) 461.
7 E. R. COREY, L. F. DAHL AND W. BECK, *J. Amer. Chem. Soc.*, 85 (1963) 1202.
8 P. CHINI AND S. MARTINENGO, *Chem. Commun.*, (1968) 251.
9 P. CHINI, private communication.
10 P. CHINI AND S. MARTINENGO, in press.
11 P. CHINI, private communication.
12 J. HORNSTRA, *Report 4021*, N. V. Philips Gloeil. Fabr., Eindhoven, 1965.
13 W. R. BUSING AND H. A. LEVY, *Acta Crystallogr.*, 10 (1957) 180.
14 W. L. BOND, *Acta Crystallogr.*, 12 (1959) 375.
15 H. HAUPTMANN AND J. KARLE, *A.C.A. Monograph*, No. 3, 1953.
16 D. W. J. CRUICKSHANK AND D. E. PILLING, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon Press, London, 1961.
17 L. H. THOMAS AND K. UMEDA, *J. Chem. Phys.*, 26 (1957) 239.
18 R. MCWEENY, *Acta Crystallogr.*, 4 (1951) 513.
19 P. A. AGRON, R. D. ELLISON AND H. A. LEVY, *Acta Crystallogr.*, 23 (1967) 1079.
20 *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962.
21 O. S. MILLS AND E. F. PAULUS, *J. Organometal. Chem.*, 10 (1967) 331.
22 O. S. MILLS AND J. P. NICE, *J. Organometal. Chem.*, 10 (1967) 337.
23 O. S. MILLS AND E. F. PAULUS, *Chem. Commun.*, (1967) 643.
24 C. H. WEI, G. R. WILKES AND L. F. DAHL, *J. Amer. Chem. Soc.*, 89 (1967) 4792.
25 R. MASON AND A. I. M. RAE, *J. Chem. Soc., A*, (1968) 778.
26 R. MASON AND W. R. ROBINSON, *Chem. Commun.*, (1968) 468.