Inorganica Chimica Acta, 27 (1978) 233–242

The Crystal and Molecular Structure of Tetra-μ-chloro-tetra-μ-ethyloxycarbene-di-μ_3-hydroxo dodecacarbonyl-di-chloro-hexaruthenium(II)

S. MERLINO

Istituto di Mineralogia, Università di Pisa, via S. Maria 53, 56100 Pisa

G. MONTAGNOLI

Laboratorio per lo Studio delle Proprietà Fisiche di Biomolecole e Cellule, C.N.R., via F. Buonarroti 9, 56100 Pisa

G. BRACA and G. SBRANA

Istituto di Chimica Organica Industriale, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy

Received August 8, 1977

The crystal and molecular structure of tetra-μ-chloro-tetra-μ-ethyloxycarbene-di-μ_3-hydroxo-dodecacarbonyl-di-chloro-hexaruthenium(II)-benzene, $[Ru_3Cl_3(COC_2H_5)_2(OH)(CO)_6]_2 \cdot C_6H_6$, have been determined. The complex crystallizes as monoclinic crystals in space group P $2_1/c$ with unit cell dimensions a = *10.71(2)* Å, b = *10.41(2)* Å, c = *21.92(3)* Å, β = *113° 15' (10') and Z = 2. A three-dimensional X-ray analysis, based on 3101 observed reflections, converged to a* R *of 0.076. The crystal structure of the complex consists of centrosymmetric hexanuclear molecules. The three ruthenium atoms of the asymmetric unit are octahedrally coordinated. The octahedra share a common vertex occupied by a hydroxo group which bridges three ruthenium atoms. Significant differences in the Ru–Cl bond lengths are accounted by the "*trans *influence" of the carbene nature of the C_2H_5CO groups.*

Introduction

η-Allyl ruthenium complexes of formula $RuX(C_3H_5)(CO)_3$ (X = Cl, Br) have been used as catalysts in several reactions involving unsaturated substrates [1, 2]. The reactivity with different olefinic and acetylenic ligands was also widely investigated [3].

In the course of these studies some new ruthenium complexes, obtained in crystalline and amorphous forms, by reaction of $RuCl(C_3H_5)(CO)_3$ (I) with ethylene were isolated [2].

Since the analytical and spectroscopic data (IR and ^{1}H n.m.r.) did not allow to establish exactly the nature of the products and to understand some IR and analytical differences observed for the crystalline and amorphous product, recourse was had to X-ray crystallography.

Experimental

Preparation

By reaction of I (1 g, 3.8 mmol) with ethylene under pressure (50–60 atm) at 70–80 °C for 10 h in benzene solution and by standing the reaction mixture in the autoclave at room temperature for several days, a crystalline compound (II), initially formulated as $[RuCl(COC_2H_5)(CO)_2]_n$ with solvate benzene, was obtained [Found: C, 24.57; H, 2.17; Cl, 14.3; Ru, 40.2; M(benzene, Mechrolab Osmometer), 1600. Calc. for $C_{30}H_{28}Cl_6O_{18}Ru_6$ (on the basis of the formula determined by X-ray structural data): C, 24.09; H, 1.88; Cl, 14.22; Ru, 40.55%; M, 1495.7]. The complex could also be isolated as an amorphous product (III) either by adding n-pentane to the benzene solution or by evaporating to dryness [Found: C, 23.82; H, 2.18; Cl, 14.6; Ru, 39.2. $C_5H_5ClO_3Ru$ requires C, 24.05; H, 2.02; Cl, 14.21; Ru, 40.4%].

IR and ^{1}H n.m.r. Spectra

The IR spectra (Perkin–Elmer 225 spectrometer, in KBr) of the crystalline and amorphous products showed three bands in the carbonyl stretching region at 2130 vw, 2060vs, 2005vs cm^{-1} and the bands assignable to a bridging acyl group (1543s cm^{-1}) [4] and to the terminal (329w cm^{-1}) and bridging chlorine atoms (290w and 260w cm^{-1}) [5]. The IR spectrum of the crystalline product differed from that of the amorphous one for a weak but sharp absorption at 3280 cm^{-1} [ν(OH)], by a more complex pattern of bands in the Ru–C–O deformation and Ru–C stretching region (650–400 cm^{-1}) and by the bands due to solvate benzene.

The ^{1}H n.m.r. spectrum of the crystalline product (Varian T 60 spectrometer, in benzene solution) showed a quartet and a triplet at 7.32 and 9.15 τ

TABLE I. Positional and Thermal Parameters for Non-hydrogen Atoms in $[Ru_3Cl_3(COC_2H_5)_2(OH)(CO)_6]_2 \cdot C_6H_6$[a,b].

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	−0.08384(10)	−0.20176(11)	0.40900(5)	81.7(10)	23.3(15)	20.6(2)	−5.1(8)	17.6(4)	−3.4(4)
Ru(2)	0.06520(10)	0.02238(12)	0.34289(5)	75.0(9)	40.2(15)	19.1(2)	0.8(8)	17.1(4)	0.0(4)
Ru(3)	−0.19243(10)	0.15187(12)	0.37316(5)	70.4(9)	36.0(15)	20.4(2)	1.9(8)	14.1(4)	−1.1(4)
Cl(1)	0.13394(34)	−0.20980(38)	0.50463(16)	88.4(32)	44.7(51)	20.5(8)	9.8(28)	16.0(13)	−1.6(14)
Cl(2)	0.03363(37)	−0.21990(39)	0.33623(18)	108.0(36)	33.5(50)	25.1(9)	3.4(30)	28.4(15)	−5.8(15)
Cl(3)	−0.19267(36)	−0.15407(42)	0.48031(17)	99.0(35)	58.1(53)	23.3(8)	−4.0(32)	25.7(14)	−1.6(15)
C(1)	−0.1038(16)	−0.3769(18)	0.4170(8)	107(16)	75(26)	24(4)	−38(15)	16(6)	1(7)
C(2)	−0.2436(15)	−0.2023(16)	0.3344(8)	93(14)	47(21)	26(4)	−23(12)	27(6)	−10(6)
C(3)	0.1465(15)	0.0427(18)	0.2829(8)	90(15)	92(25)	23(4)	9(14)	14(6)	−3(7)
C(4)	0.2430(14)	0.0003(17)	0.4077(7)	84(14)	83(23)	24(4)	−7(13)	22(6)	−4(7)
C(5)	−0.3455(17)	0.0640(17)	0.3741(8)	122(19)	41(22)	30(4)	11(15)	19(7)	−6(7)
C(6)	−0.3053(15)	0.2876(17)	0.3438(7)	99(15)	93(25)	20(3)	1(14)	21(6)	6(6)
C(7)	−0.2311(14)	0.0923(16)	0.2809(6)	92(13)	56(20)	14(3)	−8(12)	9(5)	1(5)
C(8)	0.0700(11)	0.2065(15)	0.3584(6)	52(11)	67(22)	23(3)	19(10)	14(5)	6(6)
C(9)	−0.3624(15)	0.1058(19)	0.2217(8)	77(14)	108(27)	22(4)	0(14)	−1(6)	7(7)
C(10)	−0.3629(18)	0.2253(19)	0.1834(9)	136(20)	65(25)	28(5)	17(17)	20(8)	15(8)
C(11)	0.1766(15)	0.3009(18)	0.3580(8)	83(14)	101(26)	23(4)	−15(14)	17(6)	−8(7)
C(12)	0.1649(21)	0.4437(20)	0.3825(11)	166(26)	24(24)	51(8)	15(18)	31(12)	−4(9)
C(13)	0.4235(26)	0.0358(32)	0.0363(13)	171(32)	291(55)	36(7)	73(34)	14(12)	1(15)
C(14)	0.4899(34)	0.1302(29)	0.0120(13)	286(48)	165(45)	39(8)	−18(36)	14(16)	−19(14)
C(15)	0.4390(32)	−0.0909(34)	0.0246(14)	254(46)	243(53)	40(9)	−73(39)	4(16)	13(16)
O(1)	−0.1189(14)	−0.4803(14)	0.4243(7)	157(17)	86(19)	38(4)	−32(13)	29(7)	7(7)
O(2)	−0.3461(12)	−0.2025(13)	0.2887(6)	102(13)	127(20)	27(3)	−17(12)	−1(5)	−8(6)
O(3)	0.1997(12)	0.0459(14)	0.2474(6)	135(15)	148(20)	30(3)	18(13)	46(6)	9(6)
O(4)	0.3509(11)	−0.0135(13)	0.4438(6)	94(12)	130(20)	30(3)	25(12)	13(5)	8(6)
O(5)	−0.4450(11)	0.0221(13)	0.3705(7)	87(12)	107(19)	48(5)	−8(11)	35(6)	10(7)
O(6)	−0.3744(13)	0.3776(12)	0.3265(6)	151(16)	57(17)	32(3)	48(12)	17(6)	7(5)
O(7)	−0.1351(9)	0.0436(10)	0.2705(4)	82(9)	54(14)	14(2)	4(8)	8(3)	4(4)
O(8)	−0.0279(9)	0.2556(10)	0.3698(5)	78(9)	12(12)	28(3)	−8(8)	22(4)	1(4)
O(9)	−0.0431(9)	0.0020(10)	0.4069(4)	84(9)	44(13)	17(2)	7(8)	21(4)	4(4)

[a] The numbers in parentheses in this and other tables are the estimated deviations in the least significant digits. The anisotropic thermal parameters are of the form $\exp[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

from TMS, in the proper intensity ratio for an ethyl group, and a resonance at 10.9 τ assignable to a triple bridging OH group [6]. This last resonance was absent in the spectrum of the amorphous product.

X-ray Crystallography

Unit-cell dimensions and space group for the crystals of the complex II were obtained from precession photographs taken with Mo Kα radiation. The crystals belonged to the monoclinic system with a = 10.71(2) Å, b = 10.41(2) Å, c = 21.92(3) Å, β = 113° 15′ (10′). Systematic absences (h0l absent for l = 2n + 1 and 0k0 absent for k = 2n + 1) indicated space group P $2_1/c$. For Z = 2 the calculated density was 2.45 g/cm^3.

The intensity data were recorded with Ni-filtered Cu Kα radiation (λ = 1.5418 Å) by means of Weissenberg photographs with multiple film technique and integration process. A crystal elongated in the b direction was reduced to nearly cylindrical shape with a radius of 0.013 cm (μR = 2.70 for Cu Kα radiation). Nine layers with b as rotation axis (k = 0 through 8) were taken.

A total of 4138 independent reflections (3101 observed) were collected. The intensities measured with a Nonius microdensitometer have been corrected for Lorentz and polarization effects, for the incipient but incomplete $\alpha_1 - \alpha_2$ spot doubling and for the absorption factor using the three-constant formula proposed by Palm [7] for cylindrical crystals.

Solution and Refinement of the Structure

The ruthenium atoms were located from three-dimensional Patterson function. All chlorine, carbon, and oxygen atoms were located by successive Fourier syntheses. Various cycles of block-matrix least squares refinement lowered the value of $R = \Sigma \, ||F_o| - |F_c||/\Sigma|F_o|$ to 0.092: unit weights were assumed for all observed reflections, isotropic temperature factors were attributed to carbon and oxygen atoms, while anisotropic temperature factors were attributed to ruthenium and chlorine atoms.

The anisotropic refinement was extended to all the atoms and the weighting scheme $\sqrt{w} = 1/(a + |F_o| + b|F_o|^2)$ proposed by Cruickshank [8] was introduced with a = 40.0 and b = 0.005.

Seventeen strong reflections, probably affected by extinction, were excluded from the last refinement cycles. The final R value was 0.076.

Scattering factors used in the structure factor calculations were taken from International Tables for X-ray Crystallography [9]. All the programs used are incorporated in the X-ray 70 system [10]. Positional and thermal parameters for the atoms in the asymmetric unit are given in Table I. Observed and calculated structure factors are compared in Table II.

Results and Discussion

The resolution of the structure of the crystalline product II allows to formulate this as tetra-μ-chloro-tetra-μ-ethyloxycarbene-di-μ_3-hydroxo-dodecacarbonyl-dichloro-hexaruthenium(II)-benzene, $[Ru_3Cl_3(COC_2H_5)_2(OH)(CO)_6]_2 \cdot C_6H_6$.

The crystal structure of II is composed of two discrete hexanuclear molecules located at the inversion centers at (0, 0, 1/2) and (0, 1/2, 0) in the monoclinic unit cell. At another pair of centers at (1/2, 0, 0) and (1/2, 1/2, 1/2) are two molecules of benzene of crystallization.

This structure is closely analogous to that of a toluene-containing form of di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel-(II) [11] which also crystallizes in the space group P $2_1/c$ with two hexanuclear molecules at two inversion centers and two disordered molecules of toluene at another pair of centers. The resemblance goes further as both the complex molecules are composed of two trinuclear units, related by a center of symmetry and joined by two bridging water molecules in the nickel complex and by two bridging chlorine atoms in II. In both cases the three metal atoms in the asymmetric unit are each octahedrally coordinated and the three octahedra share a common vertex at the position of the hydroxo group.

Fig. 1 is an ORTEP [12] drawing of the molecule. Bond lengths and angles are given in Tables III and IV, together with their standard deviations.

As shown the molecular structure of II has a number of unusual features that seldom are present in a same molecule.

The first one is the presence of two bridging C_2H_5-CO groups between the Ru(2) and Ru(3) atoms; a similar situation was up to now found only in the crystal structure of bis-(μ-phenyloxycarbene-tricarbonyliron) [13]. In that case, however, the C atoms of the two bridging groups are both linked to the same iron atom, whereas the oxygen atoms are linked to the other iron atom. The C–O bond lengths of C_2H_5CO groups [C(7)–O(7): 1.246 Å; C(8)–O(8): 1.276 Å] longer than that of a keto group (1.23 Å) and analogous to those found in the "carbene compound" $Fe_2(CO)_6[C(O)Ph]_2$ [13] and the Ru–C distances [Ru(2)–C(8): 1.944 Å; Ru(3)–C(7): 1.996 Å], longer than the ruthenium carbonyl lengths (1.89 Å) but shorter than those of a Ru–C (σ) bond (2.07 Å) [14], indicate for the bridging C_2H_5CO groups an arrangement of carbene type [13]. The carbene character of $C_2H_5C(O)$ groups, which display a high σ-donor and a low π-acceptor power, is also evidenced by the lengthening by *trans* effect [15, 16] of the Ru(2)–Cl(2) and Ru(3)–Cl(1)^i bonds.

The C_2H_5 groups in II arise from the insertion of a C_2H_4 molecule into a ruthenium–hydrogen bond formed by β-elimination of pentadienes from the

TABLE II. Observed and Calculated Structure Factors ($\times 10^2$). The reflections marked with a star were excluded from the last refinement cycles.

5,2,L

-13	338	-316
-14	568	-1078
-15	345	-381
-16	245	-234
-20	488	461
-21	362	-327
-22	438	377
-24	286	290
-25	511	501
-26	268	-264

6,2,L

0	806	-377
1	383	-377
2	576	972
5	658	678
6	1289	-1348
7	382	380
10	711	709
12	189	-166
13	301	288
14	173	-167
17	190	-203
18	148	-169
-1	343	321
-2	297	-230
-3	1367	1324
-4	281	286
-5	868	826
-6	1324	-1263
-7	1212	-1233
-8	780	-726
-9	576	-569
-10	655	646
-11	1036	1014
-12	681	659
-13	579	581
-14	252	-235
-15	629	-625
-18	439	-439
-21	280	-287
-22	663	643
-23	241	-229
-24	220	205
-25	216	212
-26	338	-338
-27	190	197

7,2,L

3	620	591
4	289	-281
6	890	-891
7	252	-257
8	241	244
9	249	255
10	765	776
11	167	114
12	358	-401
13	160	-145
14	334	-326
15	223	-236
-1	792	-754
-2	376	328
-3	952	887
-5	1589	1598
-6	1366	-1314
-7	323	-278
-8	471	-472
-9	1049	-1031
-10	499	453
-11	390	370
-13	1115	1026
-14	325	291
-15	219	168
-17	393	-357
-18	1035	-952
-20	671	-627
-22	713	658
-24	196	184
-26	263	-266
-27	116	143

8,2,L

2	389	-356
4	213	-246
5	607	-623
6	606	-615
8	245	240
9	307	303
10	462	459
11	224	-213
12	305	-315
13	339	-376
14	225	-262
-1	717	-680
-2	915	879
-3	346	-293
-4	267	250
-5	1028	983
-6	1132	-1063
-7	501	458
-8	302	-286
-9	658	-615
-11	459	-439
-12	436	-398
-13	443	371
-14	661	625
-15	1021	963
-18	973	-918
-19	309	-276
-20	617	-575
-22	495	426
-23	316	306
-26	115	-103

9,2,L

0	307	-292
2	586	-574
3	326	-346
5	276	-264
7	196	217
9	164	156
10	229	241
11	331	-383
12	140	-181
-1	742	-205
-2	1051	985
-3	538	-505
-6	900	-841
-7	245	255
-11	771	-716
-12	400	-354
-13	624	-564
-14	685	639
-15	578	550
-16	448	446
-17	617	595
-18	615	-594
-19	330	-296
-20	376	-352
-21	263	-326
-22	163	139
-23	273	248
-25	134	148
-26	75	90

10,2,L

0	591	-579
1	297	-309
2	568	-567
4	381	389
5	136	141
6	187	179
7	247	255
9	117	-114
-2	669	651
-4	891	902
-5	882	-852
-9	372	344
-10	351	-319
-11	321	-307
-13	937	-899
-14	689	631
-16	334	314
-17	598	549
-18	398	-364
-21	384	-357
-23	191	-200
-24	155	-144
-25	128	162

11,2,L

0	300	-319
1	272	-289
2	292	-288
4	302	343
3	227	268
5	296	363
6	151	185
-1	164	-179
-2	383	365
-3	385	382
-4	169	147
-6	400	401
-7	276	-274
-8	193	174
-9	238	258
-10	792	-747
-11	186	164
-12	271	-248
-13	555	-527
-14	803	761
-15	476	-459
-16	241	219
-17	208	171
-18	279	-244
-19	234	215
-20	258	232
-21	131	-122
-23	244	-402
-24	141	-178

12,2,L

2	145	-170
-1	279	-319
-2	152	154
-3	193	194
-4	156	-158
-5	302	288
-6	394	401
-8	668	652
-10	576	-572
-11	210	211
-12	305	-309
-14	536	543
-15	218	-196
-16	136	124
-17	172	-162
-19	213	205
-20	183	212
-21	232	244
-22	103	-143

13,2,L

-3	172	-159
-4	256	-269
-6	803	386
-7	233	282
-8	488	492
-10	306	-338

-12	271	-317
-13	127	132
-14	210	238
-15	192	199
-17	144	-152
-18	82	93

0,3,L

1	1083*	1505
2	1741*	2229
3	874	950
4	816	-862
5	1019	-1128
6	509	-500
8	328	-330
9	1740	1844
10	508	-438
11	429	375
13	788	-775
14	619	602
15	654	611
16	271	-246
18	381	-342
19	761	-723
22	222	-204
23	528	543
25	73	-82

1,3,L

0	414	430
1	695	-698
2	710	681
3	908	-940
4	707	-734
5	489	-493
6	862	-848
7	203	150
9	341	322
10	303	-273
12	564	-557
13	376	-347
14	778	763
16	284	-228
18	577	-510
19	585	-525
21	291	258
22	122	141
23	422	428
-1	2619*	3429
-2	1346	-1828
-3	1979	2346
-4	571	-580
-5	1201	-1351
-6	581	-609
-7	639	-687
-8	236	200
-9	1675	1828
-10	860	839
-11	1048	1079
-12	378	-316
-13	487	-487
-14	902	-843
-15	691	660
-17	521	503
-18	373	368
-19	444	-404
-20	279	-268
-22	296	274
-23	393	352
-25	106	142
-26	154	-265

2,3,L

0	708	-665
1	2595	-2819
2	589	522
3	818	-780
4	580	-543
5	1004	998
6	981	-981
7	1041	-1026
8	213	182
9	654	-610
10	361	-335
11	778	739
13	361	-335
14	481	423
15	783	-737
17	279	-259
18	668	-619
21	270	264
22	303	322
23	115	128
-1	750	693
-2	311	-277
-3	2472	2776
-4	667	-611
-5	1506	-1669
-6	1188	-1286
-7	1863	-2234
-8	568	-590
-9	339	363
-10	1176	1287
-11	758	761
-12	239	-191
-13	570	561
-14	1133	-1137
-15	276	291
-21	460	431
-22	237	210
-26	172	-227

3,3,L

0	211	-159
1	1994	-2067
2	337	349

5	587	495
6	863	-836
7	1232	-1247
8	350	326
9	327	303
11	968	951
12	292	264
13	468	-416
15	936	-917
17	365	339
18	423	-376
19	467	459
20	141	107
21	120	-127
22	208	267
-1	1360	-1274
-2	318	301
-3	889	938
-4	890	355
-5	660	572
-6	1768	-1885
-7	887	-872
-8	652	-705
-9	1138	-1236
-10	1321	1458
-11	697	-767
-13	842	921
-14	792	-814
-15	543	557
-16	287	-226
-17	1078	-1086
-18	371	-353
-19	372	-307
-21	591	572
-22	258	219
-25	187	-197
-26	205	-249
-27	221	389

8,3,L

0	268	-237
1	648	-636
2	268	226
3	574	-536
4	872	871
5	426	395
6	851	-860
7	190	-164
8	476	435
10	648	665
11	448	395
13	698	-673
15	596	-562
17	784	824
18	154	-137
19	288	264
20	187	201
-1	801	-302
-2	1031	925
-3	801	-699
-4	848	821
-5	663	586
-6	1628	-1545
-7	798	739
-8	640	-616
-9	1718	-1925
-10	967	1079
-11	1937	-2202
-12	399	424
-13	558	599
-15	768	847
-17	853	-821
-18	468	-468
-19	733	-700
-22	806	376
-25	173	-205
-26	168	-204
-27	186	196

5,3,L

0	250	-228
2	869	883
3	842	-792
5	733	698
6	893	-857
7	958	981
8	390	358
10	717	701
11	289	-278
13	544	-545
14	322	-285
17	542	535
18	98	86
-1	888	829
-2	936	836
-3	780	-686
-4	879	816
-6	658	-573
-7	1853	1844
-8	830	-833
-9	258	-223
-10	747	698
-11	2125	-2248
-12	278	232
-13	326	311
-14	628	557
-15	950	935
-16	287	279
-17	281	-221
-18	678	-628
-19	622	-558
-21	478	-444
-22	890	876
-23	342	-331
-27	70	90

6,3,L

1	740	-713
3	990	-965
5	987	976
7	976	998
8	316	252
9	771	-789
10	562	510
11	491	-464
12	252	-201
13	263	234
14	278	-230
15	170	141
16	112	94
-1	1207	1160
-2	923	858
-3	265	-276
-4	500	459
-5	210	-198
-6	337	-290
-7	1343	1299
-9	977	951
-11	653	-648
-12	280	-282
-13	379	-382
-14	1114	1070
-15	371	333
-16	513	485
-17	646	599
-18	486	-428
-19	407	347
-21	568	-524
-22	437	382
-23	525	-518
-24	169	155
-25	327	311
-27	165	204

7,3,L

0	413	-373
1	539	-471
2	579	-561
5	967	1011
6	237	239
7	357	328
9	1122	-1182
10	232	213
11	176	-137
12	276	-270
13	569	596
-2	1060	995
-4	231	197
-5	471	410
-6	490	-429
-7	690	628
-8	220	218
-10	233	-236
-11	471	416
-12	414	-389
-14	628	582
-15	583	-532
-16	695	659
-17	692	656
-18	385	-358
-19	1215	1211
-23	636	-638
-25	262	240
-26	259	287
-27	246	365

8,3,L

0	732	-686
1	245	219
2	510	-472
3	382	358
4	237	193
5	459	463
6	384	331
9	649	-685
10	165	-119
11	138	129
13	394	376
-1	946	-918
-2	883	885
-3	837	-762
-4	554	519
-5	737	681
-6	278	-281
-7	670	627
-9	781	-706
-10	366	-312
-11	382	330
-12	469	406
-15	701	-672
-16	386	376
-19	1219	1184
-21	195	172
-22	260	-212
-23	479	-461
-24	225	-211
-26	269	324

9,3,L

0	848	-818
1	905	889
2	420	-388
3	408	372
4	326	331
5	268	-235
6	184	143
7	160	-144
8	251	-243
11	66	96
-1	649	-610
-3	1158	-1181
-4	301	329
-5	778	704
-7	763	693

-9	831	-765
-10	724	-639
-12	259	-208
-13	227	205
-14	218	158
-15	597	-562
-17	405	-356
-19	480	473
-20	180	148
-21	222	198
-22	316	-305
-24	335	-351
-25	145	-153
-26	185	209

10,3,L

0	285	-289
1	1070	1124
2	227	-174
4	284	304
5	560	-589
8	149	-193
-2	223	-194
-3	479	489
-5	325	295
-7	488	485
-8	184	172
-10	426	-380
-12	374	-330
-13	359	-272
-14	173	156
-15	444	-416
-20	195	205
-21	267	-236
-23	209	211
-24	295	-351
-25	59	-89

11,3,L

1	490	519
3	219	-226
5	268	-268
-1	149	163
-2	279	-247
-3	274	-273
-4	269	-264
-5	329	-304
-6	388	339
-7	317	-308
-8	216	211
-9	593	596
-11	673	656
-12	353	-385
-13	465	-451
-15	616	-604
-17	434	421
-20	196	194
-21	284	-291
-22	131	-119
-23	159	210

12,3,L

0	132	145
-2	139	-118
-4	709	-683
-6	1534	1615
-7	1209	1208
-8	408	-395
-9	565	-578
-10	1190	-1247
-11	1026	-1093
-12	553	526
-14	268	251
-15	759	755
-16	355	-317
-17	449	413
-19	213	207
-20	465	-528
-21	400	-462
-24	415	458
-25	375	448

0,4,L

1	1805*	-2009
2	327	-397
3	450	-393
4	929	-918
5	329	-339
6	366	302
8	872	-832
9	785	757
10	580	-556
11	885	858
12	1595	1534
13	1193	-1136
14	266	216
15	1169	-1135
16	1046	-1008
17	847	832
18	296	248
19	454	418
20	712	707
21	157	-144

1,4,L

0	1782	2020
1	1245	-1383
2	1080	1040
3	1099	-1069
4	1131	-1107
5	228	151
7	1114	1158
8	659	615
9	659	616
10	223	232
11	196	186
12	1075	1029
13	1045	-1033
16	728	-682
17	904	855
18	484	452
19	351	327
20	418	402
21	212	-160
22	231	-267
-1	839	947
-2	1661	-1781
-3	479	489
-4	324	-358
-5	212	193
-6	1348	1468
-7	1182	1278
-8	1012	-1028
-9	704	-762
-10	981	-966
-11	1868	-1833
-12	1809	1804
-13	936	887
-14	585	583
-15	1381	1371
-16	989	-950
-19	354	-310
-20	219	221
-24	114	109
-25	185	253

2,4,L

0	2190	2232
1	791	-797
2	738	-678
3	1881	-1983
4	2432	-2463
5	1791	1790
7	1729	1772
8	1544	1525
9	288	-259

5,4,L

0	1590	-1435
1	574	546
3	620	604
7	504	-508
9	753	-753
11	217	-214
12	204	-215
14	283	271
18	164	-171
-1	1184	-1146
-2	371	-285
-3	1812	-1781
-4	1743	1627
-5	1044	1030
-6	507	-469
-7	1350	1248
-8	1582	-1461
-9	413	-373
-10	390	371
-11	479	-451
-12	727	676
-14	1045	-1061
-15	553	-527
-17	231	213
-18	505	510
-19	552	557
-20	285	-281
-22	153	-123
-23	372	-402
-24	170	183
-25	113	-104

3,4,L

0	1728	1645
1	1239	-1189
3	579	-519
4	2312	-2279
5	2515	2583
6	669	653
7	1046	1056
8	1594	1603
9	1013	-1029
10	982	-981
11	395	-416
12	762	-732
13	568	525
14	390	361
16	176	161
17	182	-161
18	387	-364
19	206	200
20	188	184
21	184	-217
-2	363	376
-3	668	645
-4	287	173
-5	787	706
-6	469	418
-7	988	960
-8	1093	-1017
-9	669	-664
-10	571	538
-11	281	-280
-12	353	374
-14	524	-510
-15	254	-207
-16	412	393
-17	383	378

6,4,L

1	927	916
2	584	575
4	412	338
5	655	-651
6	593	-577
8	330	335
9	472	-452
10	314	292
11	395	-398
12	283	-276
13	254	268
16	176	163
-1	517	-492
-2	1314	-1273
-3	2294	-2201
-4	1618	1469
-5	218	-199
-6	217	222
-7	984	971
-8	1504	-1367
-11	309	-310
-13	483	-468
-14	288	-260
-15	545	-514
-16	394	384
-17	308	287
-19	340	325
-20	359	-390
-22	210	226
-26	256	-277

7,4,L		
0	224	-169
1	925	808
2	731	710
3	347	-248
4	262	258
5	356	-347
6	334	-347
8	631	649
9	256	-244
10	419	427
12	386	-423
13	354	400
15	243	256
-2	490	-439
-3	1249	-1192
-4	615	503
-5	766	-706
-6	255	224
-9	410	396
-10	190	111
-11	326	346
-12	804	-768
-13	733	-747
-15	928	-936
-16	726	744
-17	241	250
-18	280	-259
-19	308	320
-20	716	-752
-21	263	-268
-22	366	374
-23	195	229
-24	125	117
-26	307	-371

8,4,L		
1	590	556
2	192	254
8	257	249
12	339	-327
13	407	439
-1	446	414
-2	535	515
-3	220	-219
-4	351	264
-5	363	-325
-6	393	-361
-7	748	-695
-8	805	746
-9	417	372
-10	885	840
-11	1079	1050
-12	890	-878
-13	501	-471
-14	335	-297
-15	942	-943
-16	992	1001
-19	367	388
-20	555	-552
-21	222	-221
-22	244	274
-23	187	195
-26	157	-239

9,4,L		
0	310	-278
1	340	332
2	313	-233
3	390	380
4	352	359
5	167	-172
6	167	129
8	169	-176
9	106	134
10	156	-177
-1	213	210
-2	619	622
-3	501	473
-6	790	-782
-7	770	-741
-8	525	523
-10	1060	1075
-11	1271	1267
-12	598	-541
-13	277	239
-14	384	-374
-15	708	-671
-16	709	724
-17	233	-226
-18	279	269
-19	187	154
-23	189	190

10,4,L		
0	646	-653
1	373	392
2	293	-317
3	166	177
4	443	503
5	387	-397
7	138	-153
8	306	-457
-2	367	365
-3	415	395
-4	198	171
-5	306	301
-6	616	-627
-7	359	-348
-8	205	156
-10	446	429
-11	691	700
-13	582	577
-19	294	-325
-20	340	335
-21	343	348
-22	207	169
-23	395	459
-24	224	-294

11,4,L		
0	298	-327
1	177	195
2	134	-7
3	174	-190
4	221	241
-3	153	155
-6	220	-203
-7	192	-237
-10	238	-201
-12	217	-217
-13	203	228
-14	220	230
-15	443	448
-16	180	-153
-18	452	-478
-19	497	-529
-20	332	324
-22	244	310

12,4,L		
0	124	151
-1	124	118
-2	189	172
-4	250	-362
-5	190	-207
-7	196	-229
-8	133	171
-10	236	-262
-12	264	-270
-14	319	304
-15	341	362
-18	494	-525
-19	375	-440

13,4,L		
-7	183	-261
-9	313	393
-10	99	-143
-11	156	-200
-12	138	-174
-13	151	-190
-14	141	197

0,5,L		
1	1627*	-2669
2	200	-229
3	951	1145
4	278	-282
5	682	470
6	737	713
7	280	-271
8	530	453
11	1102	-1083
13	1144	-1085
14	1072	1070
15	755	723
17	569	530
18	507	-460
19	435	-415
20	330	302
21	185	-221
22	298	355
23	139	-181

1,5,L		
0	843	-972
1	1397	-1576
2	838	832
3	1380	1454
4	983	1025
5	875	895
6	448	395
7	734	-721
8	232	-219
9	246	-243
11	594	-555
12	347	341
13	556	-488
14	392	383
15	731	690
17	686	670
18	270	-214
19	485	-437
20	333	299
21	330	-348
22	158	149
-1	1491	-1735
-2	281	303
-3	537	601
-4	1793	1971
-5	414	453
-6	208	-251
-8	1124	-1149
-9	720	710
-10	632	610
-11	1398	-1422
-12	781	736
-13	1387	-1422
-14	670	-624
-15	677	648
-16	441	-388
-17	365	326
-18	239	324
-19	238	-207
-22	199	-208
-23	271	-280
-24	158	-191

2,5,L		
0	1123	-1115
1	1234	-1190
2	1529	1521
3	2077	1988
4	1083	1076
5	1520	1377
6	1193	-1178
7	1828	-1240
9	437	-405
10	857	812
14	563	-547
15	635	595
17	483	501
19	416	-425
21	225	-261
-1	873	-847
-2	800	-788
-3	178	-63
-4	1891	1905
-5	771	-775
-6	1128	1163
-7	847	921
-8	742	-760
-9	1103	1196
-11	882	-916
-12	868	866
-13	1140	-1175
-14	393	372
-15	407	336
-16	270	-268
-17	269	256
-21	237	254
-22	237	273
-23	346	-371
-24	169	-189
-25	275	-390

3,5,L		
2	888	859
3	1696	1612
4	284	-253
5	1117	1097
6	1597	-1620
7	881	-869
8	636	626
9	596	-582
10	689	665
11	768	750
12	749	-762
13	351	333
14	611	-587
15	412	378
16	522	510
17	286	275
19	406	-375
20	225	-260
-2	967	-900
-4	219	-97
-5	1226	-1206
-6	969	884
-7	1746	1758
-8	629	609
-9	1941	2025
-10	270	-218
-11	720	-718
-12	232	-259
-13	829	-891
-14	727	748
-16	664	693
-18	316	-325
-19	300	313
-21	585	627
-22	584	579
-23	305	-347
-24	168	173
-25	303	-359

4,5,L		
0	456	433
2	348	-296
3	721	650
4	644	-632
5	1146	1107
6	408	-365
7	1146	-1180
8	669	661
9	610	-604
11	728	719
12	632	-615
13	520	524
16	611	632
19	146	-148
-1	1075	1000
-3	335	-295
-4	1139	-1092
-5	1472	-1442
-6	831	-733
-7	1098	1021
-8	818	784
-9	2166	2198
-10	383	344
-11	582	-504
-12	1181	-1247
-16	917	945
-17	289	-299
-19	530	587
-20	382	-376
-21	691	779
-22	274	283
-24	348	339
-25	268	-298

5,5,L		
0	314	-227
1	340	313
2	1035	-982
3	356	289
4	357	287
5	329	301
6	519	486
7	806	-780
9	263	-281
11	685	682
13	351	347
14	212	194
15	273	-290
16	276	251
17	215	-144
18	134	-175
-1	1291	1265
-2	1165	1090
-3	747	-711
-4	779	-743
-5	1596	-1541
-6	1427	-1346
-7	763	683
-8	483	473
-9	1146	1073
-10	739	636
-12	1007	-992
-13	454	437
-14	556	-516
-16	254	238
-17	766	-789
-19	369	421
-20	283	-273
-21	696	789

6,5,L		
0	823	-775
1	436	420
2	401	-348
3	684	-641
4	949	937
5	453	-458
6	381	354
8	688	-709
9	356	-357
11	535	555
12	320	309
13	275	255
15	452	-437
16	109	-119
-1	1312	1248
-2	1066	981
-3	773	-726
-4	445	386
-5	1471	-1351
-6	769	-680
-7	383	324
-8	287	-270
-9	234	219
-10	383	302
-11	333	282
-13	723	720
-14	336	-275
-15	368	-372
-16	427	-418
-17	1027	-1063
-19	288	258
-21	539	568
-22	195	-180
-24	400	-412

7,5,L		
0	428	-361
1	347	344
2	221	230
3	905	-887
4	606	566
5	283	-281
8	659	-668
10	301	289
11	331	316
12	282	268
14	300	-334
-1	1066	1044
-3	566	-530
-4	339	334
-5	1036	-911
-6	465	427
-9	651	-609
-10	480	-455
-12	375	354
-13	1063	1077
-14	588	581
-15	469	-460
-16	400	-389
-17	1028	-1057
-18	495	-479
-20	434	430
-21	196	207
-24	439	-469
-25	178	207

8,5,L		
0	289	237
3	765	-810
5	298	-286
6	287	-232
7	238	229
8	202	-206
10	239	274
-1	679	645
-2	339	-312
-4	493	-474
-5	453	-387
-6	623	591
-8	766	750
-9	803	-808
-10	878	-872
-13	848	838
-14	864	862
-17	653	-660
-18	518	-512
-20	325	335
-21	188	-193
-22	328	330
-24	159	-113
-25	238	309

9,5,L		
0	677	731
2	300	-274
3	640	-673
4	406	-443
5	193	-193
7	425	462
8	132	149
-1	300	290
-4	952	-945
-5	368	376
-7	235	-287
-8	851	834
-9	870	-899
-10	529	-496
-12	433	-424
-13	617	629
-14	394	397
-16	320	327
-17	171	-191
-18	186	-180
-21	428	-469
-22	149	168
-24	173	214

10,5,L		
0	423	516
2	481	-514
3	341	-380
6	407	440
7	233	379
-2	355	340
-4	635	-646
-5	563	578
-6	309	-283
-8	290	292
-9	715	-765
-12	239	-233
-13	520	516
-14	195	-190
-18	281	296
-21	450	-475
-22	268	-277

11,5,L		
2	218	-231
-1	168	-204
-2	217	238
-5	510	596
-8	238	-263
-9	401	-446
-12	299	305
-13	161	181
-14	184	-170
-16	518	-529
-17	383	374
-18	289	281
-20	134	127
-21	237	-338

12,5,L		
-2	111	-133
-4	183	194
-5	512	569
-6	373	374
-7	132	151
-8	346	-340
-9	182	-178
-10	157	-129
-12	478	475
-16	354	-399
-17	355	452

0,6,L		
1	263	372
2	356	450
3	1190	1408
4	1196	-1309
6	250	216
7	1278	-1269
8	633	615
9	963	-943
10	189	-180
11	533	482
19	238	-264
21	441	-474

1,6,L		
0	1008	1134
1	623	713
2	679	-703
4	973	-943
5	784	-725
6	738	722
7	885	-881
8	260	262
9	899	-852
10	787	-765
11	343	319
13	423	386
14	415	389
15	324	-265
16	489	-470
18	451	-444
19	296	-258
20	220	193
21	422	-425
-1	264	247
-2	719	771
-3	1939	-2283
-4	356	-373
-5	986	-1076
-6	414	-406
-7	842	844
-9	909	894
-10	716	690
-11	379	-384
-12	679	649
-13	469	-446
-14	383	-359
-16	251	-178
-17	521	-474
-18	471	430
-19	214	236
-21	376	430
-22	225	-264

2,6,L		
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4	626	-558
5	438	-378
6	289	294
7	405	-349
8	213	-197
9	834	-811
10	549	-496
11	253	252
12	260	238
13	723	679
14	339	319
15	228	-214
16	561	-561
17	417	-423
18	161	-142
19	188	-166
20	449	486
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-2	201	185
-3	1214	-1242
-4	1080	1045
-5	2292	-2436
-6	494	-469
-8	1125	-1113
-9	651	637
-10	469	444
-12	1112	1114
-13	576	-548
-14	390	-327
-15	607	-559
-16	487	-488
-17	640	-600
-18	618	572
-20	180	219
-21	162	170
-22	152	-220

3,6,L		
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1	670	582
2	379	346
3	1030	-944
4	204	83
6	555	-546
8	233	170
9	432	-368
10	240	215
11	467	471
12	180	166
13	699	644
15	243	-233
16	312	-301
17	660	-718
18	227	227
19	115	154
20	261	413
-1	904	859
-2	669	-614
-3	198	113
-4	1302	1223
-5	1802	-1743
-6	189	148
-7	839	-761
-8	1843	-1964
-10	402	-413
-11	776	820
-12	979	1003
-13	303	295
-15	951	-943
-16	589	-581
-17	790	-787
-20	170	185
-21	149	142

4,6,L		
1	1170	1101
2	1168	1102
3	749	-676
4	442	-362
5	574	-560
6	654	-621
7	359	345
8	875	855
10	623	610
11	437	427
12	334	-311
13	536	514
14	228	-221
15	487	-508
16	175	187
17	448	-452
18	156	187
-1	782	729
-2	1266	-1191
-3	177	159
-4	604	532
-5	263	192
-6	1026	949
-7	790	-753
-8	984	-906
-9	811	-717
-10	711	-685
-11	931	905
-13	1085	1041
-14	224	236
-15	542	-541
-17	818	-844
-18	410	-446
-20	280	-301
-21	220	254
-22	182	221
-24	147	165

5,6,L		
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2	723	641
3	553	-526
4	534	-489
5	872	-830
7	465	448
8	795	780
9	680	691
11	209	178
12	575	-627
15	322	-325
16	360	391
-1	671	623
-2	215	-193
-4	280	259
-5	942	828
-6	393	330
-7	234	-102
-8	317	331
-9	1100	-1032
-11	429	435
-12	520	-506
-13	1604	1631
-16	568	566
-17	353	-324
-19	263	-279
-20	589	-637
-23	203	228
-24	227	257
-25	160	244

6,6,L		
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5	795	-752
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8	336	318
9	762	819
10	296	-302
11	285	-292
12	478	-512
13	316	-286
14	219	232
-1	341	270
-2	426	393
-3	233	155
-4	597	500
-5	909	985
-6	384	-304
-8	311	261
-9	753	-728
-10	813	733
-12	362	-324
-13	871	875
-14	286	-260
-15	661	654
-16	707	703
-17	202	222
-18	322	324
-19	380	-327
-20	431	-460
-21	217	-246
-23	357	395
-24	151	174
-25	264	441

7,6,L		
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3	505	-480
4	459	449
5	374	-346
7	790	825
8	208	-215
9	434	422
10	166	-158
11	569	-587
13	99	-110
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-3	426	470
-4	702	656
-5	922	867
-6	667	-607
-7	490	-470
-8	283	-263
-9	538	-516
-10	845	819
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-15	532	531
-16	336	348
-17	537	565
-18	360	323
-21	574	-582
-23	246	236

8,6,L		
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6	359	-408
7	404	432
8	358	-416
10	187	230
11	334	-474
-1	519	-534
-3	652	645
-4	540	517
-5	613	592
-6	353	-315
-7	519	-501
-8	475	-467
-9	467	-437
-13	457	-460
-17	572	619
-20	309	312
-21	583	-607
-22	143	166
-24	149	-209

9,6,L		
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1	448	-500
2	393	424
3	327	354
4	281	333
5	142	172
6	396	-438
8	107	-131
-1	922	-963
-2	262	-262
-3	460	451
-5	695	713
-7	407	-412
-9	252	-210
-10	400	-408
-12	361	-360
-13	498	-544
-14	297	316
-17	377	425
-18	479	-544
-21	312	-341
-22	274	311
-23	150	-224

10,6,L		
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-4	339	-335
-5	456	486
-8	587	637
-10	222	-225
-11	312	-322
-12	558	-602
-13	394	-432
-14	253	275
-16	222	211
-17	226	230
-18	440	-449
-20	161	-161

11,6,L		
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-5	160	-168
-6	218	-202
-7	292	303
-8	526	570
-9	417	443
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-12	333	-356
-13	518	-553
-14	153	165
-15	192	189
-16	206	200
-17	249	261
-18	127	-90
-19	95	-112

12,6,L		
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-6	161	-226
-9	579	644
-10	115	168
-13	520	-568

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4	1034	-1083
5	212	146
6	552	-547
7	1268	-1243
8	1000	930
10	264	249
11	1285	1251
12	786	-721
13	669	608
15	400	-394
17	286	-232
19	199	206
20	274	260
21	255	346

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0	562	-649	0	1256	-1228	8	481	-520	-20	106	180	-19	352	490	10	625	620	-16	232	-193	-10	469	461
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4	941	-903	4	980	908	15	304	-354				-1	238	-441	-1	308	279	-22	132	183	-17	220	-225
5	772	-727	5	338	-281	16	135	219	0	225	194	-3	233	-271	-2	694	-640				-18	272	-325
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-13	902	862	-14	601	-579	2	336	318	-19	229	247	7	646	530	3	615	-529	-14	455	-493	-15	573	-194
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-17	660	-639	-17	229	200	5	580	573				11	738	636	7	403	349	-19	527	613			
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-21	335	408	-20	344	-413	10	237	295	0	187	175	17	204	289	12	231	240				1	455	602
			-21	372	-408	11	182	178	1	153	149				13	331	-385		6,8,L		-2	259	299
	2,7,L					-1	388	-895	2	172	-168		1,8,L		14	334	367				-3	253	-277
				8,7,L		-3	421	-374	4	186	167				15	266	-293	4	282	-268	-4	250	238
0	926	-833				-4	511	-466	5	136	136	0	164	-211	17	319	472	5	389	370	-8	228	-227
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3	670	-606	1	1602	-1563	-6	885	-390	-2	882	876	5	2016	1859	-3	1298	-1154	9	576	-700	-10	205	-197
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6	246	227	3	1257	-1233	-8	842	790	-4	206	-171	7	283	221	-6	471	381	-1	268	-276	-14	358	380
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8	814	730	5	653	627	-11	751	-741	-6	196	-188	10	0	-795	-9	927	-808	-3	572	-505	-18	306	-387
9	1074	1057	6	833	-892	-12	767	-773	-7	200	166	11	1034	944	-11	987	-929	-5	340	326	-19	136	-199
11	584	504	7	588	572	-13	284	227	-8	265	191	14	511	466	-13	988	996	-6	757	-665			
12	719	-723	8	250	-243	-16	333	354	-9	661	711	15	589	-591	-14	428	-441	-7	262	-278		10,8,L	
13	795	-794	9	670	-667	-17	246	-229	-11	508	553	17	173	214	-15	565	635	-9	483	-452			
14	363	354	11	896	-893	-18	232	-246	-12	241	270	19	300	376	-18	342	426	-10	697	632	-1	181	241
15	442	-450	13	238	-210	-19	180	176	-13	379	-382	-1	876	934	-19	768	395	-11	692	630	-2	206	227
16	417	425	14	249	256	-20	191	163	-14	210	203	-2	487	-534	-20	208	214	-12	310	348	-3	245	296
17	328	344	-1	848	390	-22	273	298	-15	830	-863	-3	1343	1452				-14	361	-320	-5	179	-245
18	129	-156	-2	358	914	-23	252	-303	-16	358	-429	-4	204	-278		8,8,L		-15	1292	-1358	-7	514	-570
-1	989	932	-4	960	905	-24	127	-256	-17	482	536	-5	349	291				-16	218	-185	-9	316	365
-2	217	-177	-6	251	-272				-18	263	-281	-6	526	466	0	578	494	-19	592	686	-11	419	489
-3	226	187	-7	500	-465		7,7,L		-19	506	594	-8	392	296	1	370	289	-21	312	-408	-13	337	-394
-4	1154	1239	-9	366	-360				-20	385	470	-9	557	-497	2	1224	1018	-22	322	225	-14	276	320
-5	340	-314	-10	682	555	1	755	778				-10	361	-339	3	1268	-1113				-16	261	344
-6	396	-347	-12	616	-570	3	447	429		10,7,L		-11	399	-356	5	268	225		7,8,L		-17	227	400
-8	589	-575	-14	258	-291	4	183	189				-12	312	-287	6	611	-533						
-9	385	-305	-16	394	393	5	196	177	0	258	301	-13	826	743	7	781	750	1	513	580		11,8,L	
-10	524	521	-17	442	441	7	291	329	2	128	-152	-14	407	-271	9	563	-567	3	557	567			
-11	558	-502	-21	419	-480	8	362	-423	3	98	192	-17	425	-550	11	526	-594	4	302	-290	-7	376	-668
-12	353	-325	-23	272	-312	10	161	164	-1	258	-291	-18	345	358	14	203	278	5	233	-287	-11	307	534
-13	513	472	-24	151	-210	-1	472	-437	-4	178	-178	-19	260	310	15	178	233	6	232	-231			
-14	573	-536				-2	355	355	-6	180	133				-1	372	274	7	248	-286			
-15	881	872		5,7,L		-3	890	-831	-7	807	-464		2,8,L		-2	805	-647	9	178	-219			
-16	740	699				-4	738	-673	-10	177	-188				-3	1636	-1445	10	131	158			
-17	422	-404	0	847	-787	-5	770	743	-11	628	769	0	193	117	-4	308	-284	-1	616	-568			
-18	301	278	1	1329	-1300	-6	675	-641	-12	330	392	1	462	-372	-5	529	-453	-2	477	482			
-19	793	-815	2	357	357	-7	1178	1156	-13	185	-166	5	1436	1249	-7	1667	1565	-3	541	-485			
-20	524	-661	3	332	-264	-8	804	765	-14	350	419	6	521	411	-8	478	416	-5	865	874			
-23	259	386	4	985	815	-11	647	-645	-15	588	-642	9	396	-383	-10	513	491	-6	855	-818			

alkyl intermediate derived by a primary insertion of ethylene into a ruthenium–allyl bond of I [2].

The second feature is the presence of a triple bridging hydroxo group: such a group has been previously characterized in the crystal structure of $[Pt(OH)(CH_3)_3]_4$ [17,18], $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ [11] and $[W(OH)(CO)_3H]_4 \cdot 4\ OPPh_2Et$ [19]. As the hydroxo group is a five-electron donor, in one molecule of II there are a total of sixty ligand-donated electrons, so each ruthenium atom can conform to the closed shell configuration without any metal–metal bond.

The close approach O(9)...Cl(3)^{i} [3.174(9) Å] between the oxygen of the hydroxo group and the terminal chlorine atom is indicative of hydrogen bonding: as appears from Fig. 1, the relative orientation of the two atoms is favourable for hydrogen bonding which assures a further linking between the two centrosymmetrically related trinuclear units in the molecule. This is also confirmed by the sharp IR absorption at 3280 cm^{-1}, consistent with the O–H stretching frequency for an O...Cl bond distance of 3.19 Å [20]. The origin of the hydroxo group of II, indicated also by a resonance at 10.9 τ in the ^1H n.m.r. spectrum [6], is not clear: it might arise from the moisture of the commercial ethylene used as well as from decomposition of carbon monoxide [21].

The last feature of the molecular structure of II is the different coordination of the three ruthenium atoms in the asymmetric unit: in fact, Ru(2) and Ru(3) are identically coordinated, each being linked to two carbonyl groups, to the "carbene atom" of one ethyloxycarbene group and to the oxygen atom of the other ethyloxycarbene group, to a bridging chlorine atom and to the triple bridging hydroxo group. Ru(1) on the contrary is linked to three chlorine

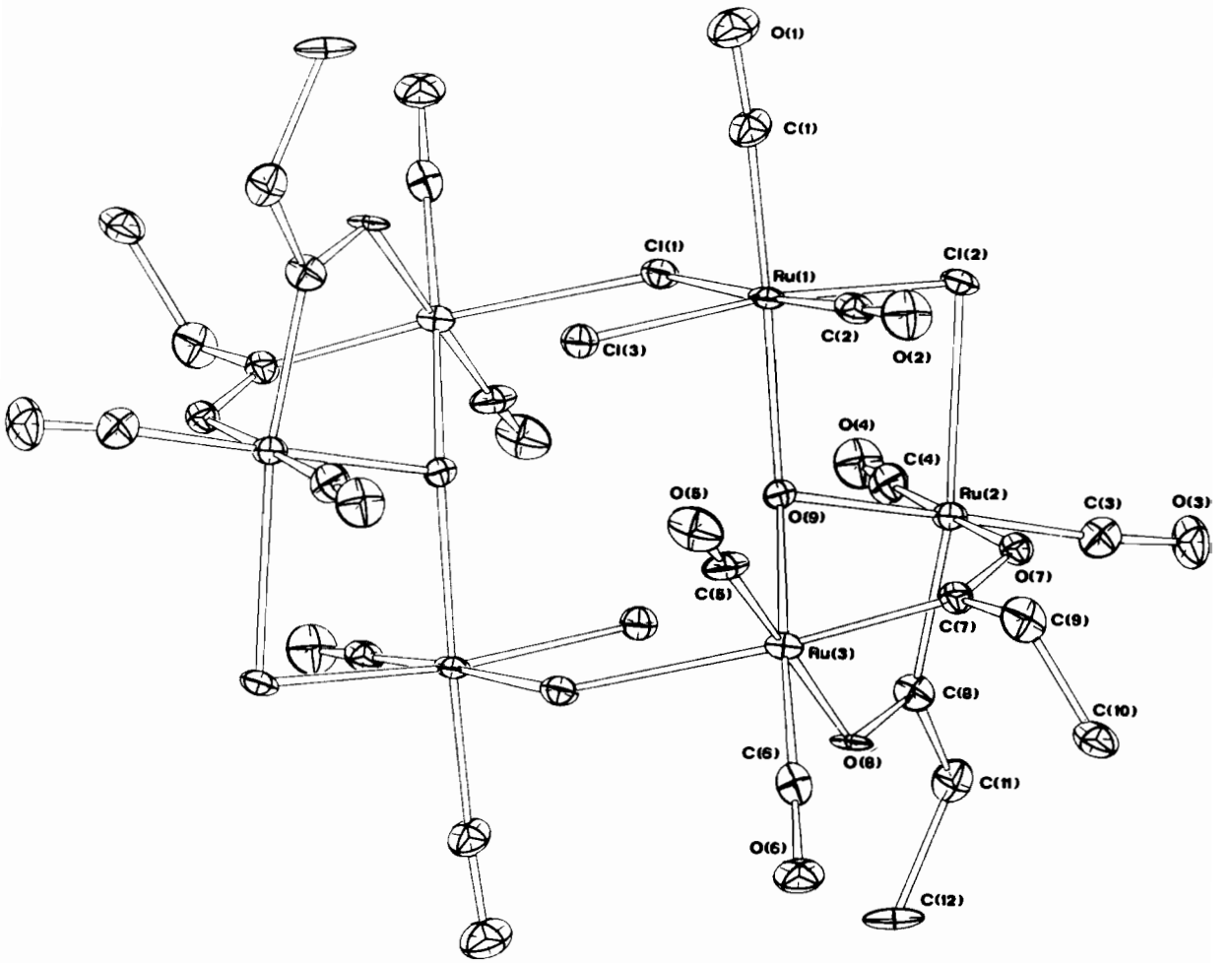


Figure 1. The molecular structure of $[Ru_3Cl_3(COC_2H_5)_2(OH)(CO)_6]_2 \cdot C_6H_6$.

TABLE III. Bond Distances (Å)[a,b].

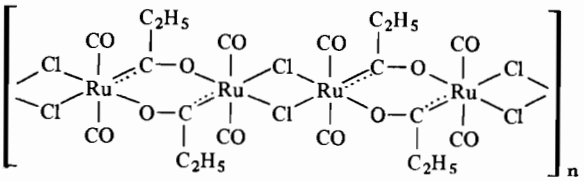
Ru(1)–Cl(1)	2.446(3)	Ru(3)–O(8)	2.094(10)
Ru(1)–Cl(2)	2.398(5)	Ru(3)–O(9)	2.146(9)
Ru(1)–Cl(3)	2.343(5)		
Ru(1)–C(1)	1.851(19)	C(1)–O(1)	1.109(24)
Ru(1)–C(2)	1.842(12)	C(2)–O(2)	1.158(16)
Ru(1)–O(9)	2.169(10)	C(3)–O(3)	1.134(25)
		C(4)–O(4)	1.123(16)
Ru(2)–Cl(2)	2.541(4)	C(5)–O(5)	1.125(23)
Ru(2)–C(3)	1.854(20)	C(6)–O(6)	1.162(21)
Ru(2)–C(4)	1.887(13)	C(7)–O(7)	1.246(19)
Ru(2)–C(8)	1.944(16)	C(8)–O(8)	1.276(19)
Ru(2)–O(7)	2.118(8)	C(7)–C(9)	1.497(17)
Ru(2)–O(9)	2.155(11)	C(9)–C(10)	1.499(28)
		C(8)–C(11)	1.509(23)
Ru(3)–Cl(1)[i]	2.571(4)	C(11)–C(12)	1.602(29)
Ru(3)–C(5)	1.885(19)	C(13)–C(14)	1.43(5)
Ru(3)–C(6)	1.805(17)	C(13)–C(15)	1.37(5)
Ru(3)–C(7)	1.996(14)	C(14)–C(15)[ii]	1.37(5)

[a]The figures in parentheses are the estimated standard deviations. [b]The symmetry code used in this and in the subsequent table is the following:

i atom at $-x \quad -y \quad 1-z$
ii atom at $1-x \quad -y \quad -z$

atoms (one terminal and two bridging), to two carbonyl groups and to the triple bridging hydroxo group.

Concerning the structure of the amorphous product, the IR spectrum does not show the presence of the triple bridging OH group and indicates a simpler arrangement of the CO groups as results from the lower Ru–C stretchings between 650 and 400 cm^{-1}. The high value of the molecular weight (~2000) furthermore suggests for this product a "*μ-catena*" arrangement of $RuCl(COC_2H_5)(CO)_2$ units of type:



Both the crystalline and amorphous products are stable in the solid state and give by treatment with

TABLE IV. Bond Angles (°)[a].

Bond Angles at the Ruthenium Atoms			
Cl(1)–Ru(1)–Cl(2)	89.7(1)	O(9)–Ru(2)–C(8)	88.1(6)
Cl(1)–Ru(1)–Cl(3)	89.6(1)	C(4)–Ru(2)–O(7)	178.9(11)
Cl(1)–Ru(1)–C(1)	89.5(4)	C(4)–Ru(2)–C(3)	86.0(7)
Cl(1)–Ru(1)–C(2)	176.6(5)	C(4)–Ru(2)–C(8)	92.2(6)
Cl(1)–Ru(1)–O(9)	85.4(2)	O(7)–Ru(2)–C(3)	94.4(5)
Cl(2)–Ru(1)–Cl(3)	172.3(2)	O(7)–Ru(2)–C(8)	88.7(4)
Cl(2)–Ru(1)–C(1)	95.5(6)	C(3)–Ru(2)–C(8)	91.4(8)
Cl(2)–Ru(1)–C(2)	87.6(6)		
Cl(2)–Ru(1)–O(9)	84.2(3)	O(9)–Ru(3)–Cl(1)^{i}	88.3(3)
Cl(3)–Ru(1)–C(1)	92.2(6)	O(9)–Ru(3)–C(5)	100.2(6)
Cl(3)–Ru(1)–C(2)	93.4(6)	O(9)–Ru(3)–C(7)	87.2(5)
Cl(3)–Ru(1)–O(9)	88.0(3)	O(9)–Ru(3)–C(6)	174.4(7)
C(1)–Ru(1)–C(2)	88.8(6)	O(9)–Ru(3)–O(8)	82.2(4)
C(1)–Ru(1)–O(9)	174.9(4)	Cl(1)^{i}–Ru(3)–C(5)	87.6(6)
C(2)–Ru(1)–O(9)	96.2(6)	Cl(1)^{i}–Ru(3)–C(7)	175.2(5)
		Cl(1)^{i}–Ru(3)–C(6)	92.4(5)
Cl(2)–Ru(2)–O(9)	81.2(3)	Cl(1)^{i}–Ru(3)–O(8)	93.1(3)
Cl(2)–Ru(2)–C(4)	89.7(5)	C(5)–Ru(3)–C(7)	91.6(7)
Cl(2)–Ru(2)–O(7)	89.3(3)	C(5)–Ru(3)–C(6)	85.4(8)
Cl(2)–Ru(2)–C(3)	99.3(6)	C(5)–Ru(3)–O(8)	177.6(5)
Cl(2)–Ru(2)–C(8)	169.2(6)	C(7)–Ru(3)–C(6)	92.3(7)
O(9)–Ru(2)–C(4)	98.1(6)	C(7)–Ru(3)–O(8)	88.0(5)
O(9)–Ru(2)–O(7)	81.5(4)	C(6)–Ru(3)–O(8)	92.2(6)
O(9)–Ru(2)–C(3)	175.9(6)		
Bond Angles in the Ligands			
Ru(1)–Cl(1)–Ru(3)^{i}	130.0(2)	Ru(2)–O(7)–C(7)	124.7(8)
Ru(1)–Cl(2)–Ru(2)	88.7(1)	Ru(3)–C(7)–O(7)	117.2(8)
Ru(1)–C(1)–O(1)	176.1(19)	Ru(3)–C(7)–C(9)	126.7(12)
Ru(1)–C(2)–O(2)	178.1(17)	O(7)–C(7)–C(9)	116.1(13)
Ru(2)–C(3)–O(3)	174.8(16)	C(7)–C(9)–C(10)	110.9(12)
Ru(2)–C(4)–O(4)	176.6(17)	Ru(3)–O(8)–C(8)	124.7(10)
Ru(3)–C(5)–O(5)	172.5(15)	Ru(2)–C(8)–O(8)	117.5(11)
Ru(3)–C(6)–O(6)	177.6(13)	Ru(2)–C(8)–C(11)	127.5(12)
Ru(1)–O(9)–Ru(2)	106.0(4)	O(8)–C(8)–C(11)	115.0(14)
Ru(1)–O(9)–Ru(3)	126.1(4)	C(8)–C(11)–C(12)	116.3(16)
Ru(2)–O(9)–Ru(3)	103.0(4)		
Bond angles in the Benzene Molecule			
C(14)–C(13)–C(15)	118.6(31)		
C(13)–C(14)–C(15)^{ii}	119.1(29)		
C(13)–C(15)–C(14)^{ii}	122.3(33)		

[a]The numbers in parentheses are the corresponding standard deviations.

triphenylphosphine or pyridine, with releasing of carbon monoxide and breaking of the bridging structure, the same mononuclear compounds $Ru(COC_2H_5)(CO)L_2Cl \cdot Sv$ (L = PPh_3, Py; Sv = benzene, methylene chloride, tetrahydrofuran) [2].

Acknowledgements

The financial support of C.N.R. (Rome) is gratefully acknowledged.

References

1 G. Braca, G. Sbrana and E. Benedetti, *Proc. Symposium on Chemistry of Hydroformylation and Related Reactions*, Veszprem (Hungary), 31th May (1972) p. 127.
2 G. Braca and G. Sbrana, *Chim. Ind., 56*, 110 (1974).
3 G. Sbrana, G. Braca and E. Benedetti, *J. Chem. Soc. Dalton*, 754 (1975).
4 E. O. Fischer and V. Kiener, *J. Organometal. Chem., 23*, 215 (1970).
5 E. Benedetti, G. Braca, G. Sbrana, F. Salvetti and B. Grassi, *J. Organometal. Chem., 37*, 361 (1972).

6 G. L. Morgan, R. D. Rennick and C. Chu Soong, *Inorg. Chem., 5,* 372 (1966).
7 J. H. Palm, *Acta Cryst., 17,* 1326 (1964).
8 D. W. J. Cruickshank, "Computing Methods in Crystallography", Pergamon Press, Oxford (1965).
9 "International Tables for X-ray Crystallography", vol. III, Kynoch Press, Birmingham (1962).
10 J. M. Stewart, "X-ray System for Crystallographic Computing", Computer Science Centre, Univ. of Maryland (1970).
11 F. A. Cotton and B. H. C. Winquist, *Inorg. Chem., 8,* 1304 (1969).
12 C. K. Johnson, ORTEP, "Oak Ridge National Laboratory", Report ORNL-3794 (1965).
13 P. F. Lindley and O. S. Mills, *J. Chem. Soc. A,* 1279 (1969).
14 M. Evans, M. Hursthouse, E. W. Randall and E. Rosemberg, *Chem. Comm.,* 545 (1972).
15 F. R. Hartley, *Chem. Soc. Rev., 2,* 63 (1973).
16 R. Mason and A. D. C. Towl, *J. Chem. Soc. A,* 1601 (1970).
17 T. G. Spiro, D. H. Templeton and H. Zalkin, *Inorg. Chem., 7,* 2165 (1968).
18 H. S. Preston, J. C. Mills and C. H. L. Kennard, *J. Organometal. Chem., 14,* 447 (1968).
19 V. G. Albano, G. Ciani, M. Manassero and M. Sansoni, *J. Organometal. Chem., 34,* 353 (1972).
20 K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc., 77,* 6480 (1955).
21 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A,* 2865 (1968).