Table 6. *Significant intermolecular contacts between atoms*

Br---C(6) (vi)	3·65 Å	O—C(1) (iii)	3·26 Å
Br—C(8)$^+$ (iv)	4·03	O—Br (iii)	3·77
Br---C(7) (vi)	3·60	O---C(1)$^+$ (iii)	3·35
C(1)–C(8)$^+$ (iv)	4·00	C(5)–C(5) (i)	3·75
Br---O (iv)	3·77	C(5)–C(6)$^-$ (i)	3·77
C(1)–O (iv)	3·26	C(6)–C(5) (i)	3·77
C(1)–O$^+$ (iv)	3·35	C(6)–Br (v)	3·65
O—C(4)$^+$ (iii)	3·41	C(7)–Br (v)	3·60
C(7)–C(7)$^-$ (ii)	4·23	C(8)–C(7)$^-$ (ii)	4·16
C(4)–O$^+$ (iv)	3·41	C(8)–Br$^-$ (iii)	4·03

Key to symmetry related atoms:

(i)	$\frac{1}{2}-x,\ 1+\bar{y},\ \frac{1}{2}+z$	(iv)	$-\frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z}$
(ii)	$\frac{3}{2}-x,\ 1+\bar{y},\ \frac{1}{2}+z$	(v)	$1+\bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z$
(iii)	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z}$	(vi)	$1+\bar{x},\ -\frac{1}{2}+y,\ \frac{1}{2}-z$

+ refers to an atom displaced one unit along the positive *c* direction.

− refers to an atom displaced one unit along the negative *c* direction.

The equation of the plane through the non-ring light atoms C(1), 0, C(2) is

$$X-3\cdot11947\ Y+5\cdot44647\ Z+4\cdot10425=0\ . \qquad (2)$$

Planes (1) and (2) make an angle of 3° 30′ with each other. The direction cosines of the normals to plane (1) are $l=0\cdot1972$, $m=-0\cdot4479$ and $n=0\cdot8720$. Those for plane (2) are $l=0\cdot1573$, $m=-0\cdot4908$ and $n=0\cdot8569$.

Table 7. *Deviations of various atoms from plane* (I)

O	0·081 (47) Å	C(4)*	0·035 (63) Å
C(1)	−0·037 (65)	C(5)*	−0·002 (66)
C(2)	0·056 (73)	C(6)*	0·032 (69)
Br	−0·124 (8)	C(7)*	−0·051 (75)
C(3)*	−0·029 (52)	C(8)*	0·057 (79)

* Atoms of the benzene ring.

Description of the structure

Figs. 3 and 4 give views of the crystal structure projected down the [001] and the [100] axes of the unit cell. In the crystal, molecules are arranged in two distinict layers inclined towards each other at an anle of about. 122°, the two layers being separated by $\frac{1}{2}c$ translation. The Br–C distance (1·929 Å) is normal. The angle Br–C(1)–C(2) is 111·5°, *i.e.* close to the, tetrahedravalue. suggesting that the atoms Br, C(2), and two hydrogen atoms conforming to a tetrahedral configuration are attached to the carbon atom C(1).

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS. A Fortran Crystallographic Least-Squares Program.* USAEC. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee. (CDC-3600 version incorporates modifications by W. C. Hamilton, J. A. Ibers, C. K. Johnson & S. Srikanta.)

International Tables for X-ray Crystallography (1952) Vol. I, Space group No. 19. Birmingham: Kynoch Press.

Acta Cryst. (1971). B27, 1653

The Crystal and Molecular Structure of Dichloro(2,7-dimethyl-octa-2,6-diene-1,8-diyl)ruthenium(IV) Dimer

By A. Colombo and G. Allegra

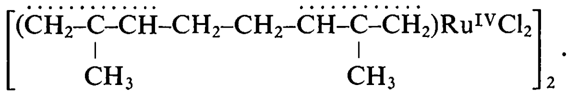
Istituto di Chimica delle Macromolecole del C.N.R., and Istituto di Chimica Industriale del Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 *Milano, Italy*

(*Received* 7 *August* 1970)

The crystal structure of $[Ru(IV)Cl_2C_{10}H_{16}]_2$ is reported and discussed. The space group is $P\bar{1}$, with $a=9\cdot49$ (2), $b=8\cdot48$ (2), $c=7\cdot71$ (2) Å, $\alpha=107\cdot8$ (2), $\beta=76\cdot6$ (2), $\gamma=100\cdot1$ (2)° and one molecule per unit cell. The final disagreement index R is 0·082 for the 1008 observed reflexions (0·105 if the 342 non-observable reflexions are taken into account). The coordination around the metal atom may be described in terms of a trigonal bipyramid, two of the equatorial positions being occupied by the terminal allylic group of the organic ligand: this corresponds to a linear tail-to-tail dimer of isoprene.

Introduction

In 1965, Porri & Gallazzi prepared a complex from $RuCl_3$ and isoprene, having the formula



$$\left[(\overset{\cdots\cdots\cdots}{\mathrm{CH_2{-}\underset{\substack{|\\ CH_3}}{C}{-}CH}}{-}\mathrm{CH_2{-}CH_2}{-}\overset{\cdots\cdots\cdots}{\mathrm{CH{-}\underset{\substack{|\\ CH_3}}{C}{-}CH_2}})\mathrm{Ru^{IV}Cl_2}\right]_2 .$$

(I)

From chemical, nuclear magnetic resonance and X-ray evidence, the compound was shown to be dimeric, and the organic ligand to be a linear tail-to-tail dimer of isoprene (Porri, Gallazzi, Colombo & Allegra, 1965). As shown in Fig. 1, the metal atom coordinates to the organic ligand *via* σ–π bonding with two terminal allyl groups; to the best of our knowledge this type of coordination has only been described for $RuCl_2C_{12}H_{18}$, where the organic ligand is the linear trimer of butadiene (Lydon, Nicholson, Shaw & Truter, 1964; Lydon & Truter, 1968). The purpose of this paper is to give the details of the X-ray structure of (I).

Experimental

Red-brown, well formed, air stable single crystals of (I) were obtained by maintaining a solution of $RuCl_3$ in ethanol (0·1g in 2 cm^3) with a large excess (10 cm^3) of isoprene at a temperature of 60–70°C for 40 hours (Porri *et al.*, 1965), and then slowly cooling the reacted mixture.

X-ray intensities were collected with the multiple-film equi-inclination Weissenberg technique, and Mo $K\alpha$ radiation. The integrated intensities of 1124 non-zero reflexions were estimated visually on the ($hk0$), ($h0l$), ($h1l$), ($0kl$) and ($1kl$) layers. No absolute scaling of the reflexions was performed at this stage; the scaling factors of the various layers were determined subsequently as adjustable parameters during the least-squares refinement. Eventually, the structure factors of the reflexions common to different layers were averaged; the resulting number of distinct reflexions was 1008. No absorption factor was applied, on account of the small size and of the regular, cubic shape of the crystal ($\mu R < 1$). The parameters of the triclinic unit cell were measured on the three equatorial layer Weissenberg photographs, calibrated with a powder spectrum of LiF; they are reported in Table 1.

Table 1. *Crystal data*

$(RuCl_2C_{10}H_{16})_2$ M.W. 616·5
a = 9·49 (2) Å
b = 8·48 (2)
c = 7·71 (2)
α = 107·8 (2)°
β = 76·6 (2)
γ = 100·1 (2)
V = 565 (3) Å^3
Z = 1
D_{exp} = 1·80 g.cm^{-3}
D_{calc} = 1·82

Table 1 (*cont.*)

No absent reflexions
Space group $P1$ or $P\bar{1}$

Small changes of the above parameters from those reported in the preliminary communication (Porri *et al.*, 1965) are due to more accurate measurements.

Structure determination

From Patterson projections along the a and the c axes we were able to locate the Ru and Cl atoms; their posi-

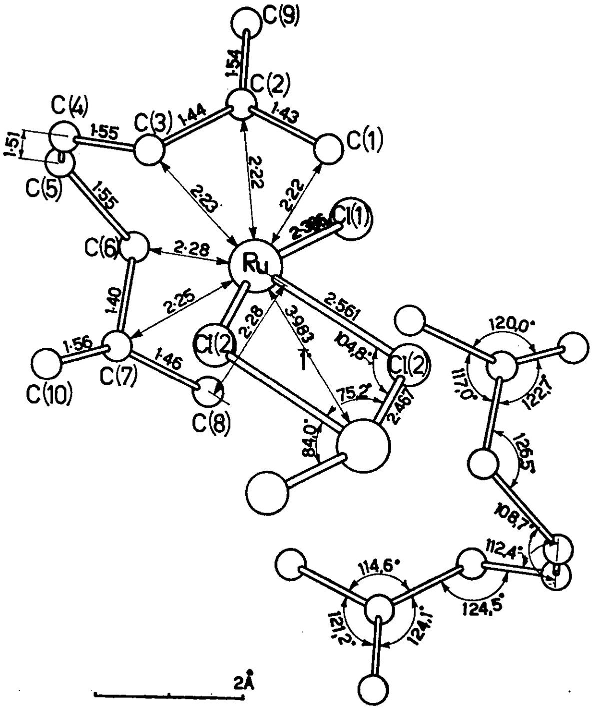


Fig. 1. Representation of the molecule seen along the crystallographic axis a. Bond distances and valence angles are reported. Standard deviations estimated for Ru–Ru, Ru–Cl Ru–C, C–C bonds respectively are 0·010, 0·007, 0·02, 0·03 Å; the first two σ's are dominated by the e.s.d. of the unit cell parameters. For angles between carbon atoms σ=0·8°, for angles involving Ru and Cl atoms, σ=0·2°.

Table 2. *Fractional coordinates, anisotropic thermal parameters and their standard deviations*

$$f_T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0·1797 (1)	0·1510 (1)	−0·0563 (1)	2·33 (4)	2·30 (4)	2·64 (4)	0·22 (5)	−0·81 (4)	0·40 (4)
Cl(1)	0·3549 (4)	0·2344 (6)	0·1412 (5)	2·9 (1)	4·0 (2)	3·1 (1)	−0·6 (2)	−1·6 (1)	1·0 (1)
Cl(2)	0·0425 (4)	−0·0100 (5)	0·1763 (4)	2·4 (1)	2·8 (1)	2·5 (1)	−0·3 (2)	−1·1 (1)	0·6 (1)
C(1)	0·056 (2)	0·354 (2)	0·142 (2)	3·7 (7)	2·6 (5)	3·0 (5)	0·3 (8)	−0·1 (6)	0·5 (5)
C(2)	0·160 (2)	0·420 (2)	0·008 (3)	2·6 (6)	2·5 (5)	4·8 (7)	1·0 (7)	0·9 (7)	1·3 (6)
C(3)	0·145 (2)	0·342 (2)	−0·181 (2)	5·3 (9)	1·7 (4)	2·7 (5)	1·0 (9)	−1·4 (6)	−0·2 (4)
C(4)	0·255 (2)	0·375 (3)	−0·353 (3)	3·8 (7)	4·8 (10)	3·8 (7)	0·5 (11)	−0·7 (7)	1·7 (8)
C(5)	0·403 (3)	0·326 (3)	−0·367 (3)	4·4 (9)	4·8 (10)	5·4 (9)	−0·4 (12)	−0·4 (9)	3·3 (9)
C(6)	0·384 (2)	0·185 (2)	−0·271 (2)	3·0 (6)	3·4 (6)	3·3 (6)	1·2 (8)	−1·2 (6)	1·3 (6)
C(7)	0·314 (2)	0·024 (2)	−0·329 (2)	1·8 (4)	3·3 (6)	3·2 (5)	1·4 (6)	−0·1 (5)	−0·3 (6)
C(8)	0·294 (2)	−0·082 (2)	−0·205 (2)	2·4 (5)	3·3 (6)	3·9 (6)	1·5 (7)	−0·1 (6)	1·4 (6)
C(9)	0·283 (2)	0·558 (2)	0·066 (3)	2·8 (6)	2·8 (6)	6·0 (9)	−0·2 (7)	0·1 (8)	0·6 (8)
C(10)	0·246 (2)	−0·038 (3)	−0·507 (2)	4·3 (8)	4·7 (8)	2·8 (5)	−0·1 (12)	−1·8 (6)	−0·3 (6)

tions corresponded to a centrosymmetric arrangement, and hence the $P\bar{1}$ space group was accepted. Then by Fourier methods we were able to locate stepwise all carbon atoms on the same projections. After the refinement, carried out through differential Fourier syntheses, the $R=(\sum||F_{\text{calc}}|-|F_{\text{obs}}||/\sum|F_{\text{obs}}|)$ index was 0·09 and 0·13 for the non-zero *hk*0 and 0*kl* reflexions, respectively.

The atomic coordinates and thermal parameters obtained represented the starting point for the overall least-squares refinement, carried out with computer programs prepared by Immirzi (1967). The weighting scheme suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted ($1/w=A+B|F_{\text{obs}}|+C|F_{\text{obs}}|^2$); a weight equal to half that corresponding to the weakest observed intensities was attributed to the non-observed reflexions. Atomic scattering factors were calculated with the analytic expression suggested by Vand, Eiland & Pepinsky (1957), adopting for the parameters the values suggested by Moore (1963). Three cycles were run in the block-diagonal approximation, assuming anisotropic thermal parameters for the Ru and Cl atoms only. Then four cycles were performed with full-matrix and anisotropic thermal parameters for all non-hydrogen atoms; the final shifts of the atomic parameters were negligibly small, all of them being well below the corresponding estimated standard deviations. The final value of the R disagreement factor was 0·082 for the 1008 observed reflexions, and 0·105 if the 342 non-observed reflexions were accounted for with a fictitious structure factor equal to 0·5 times the limit of detectability. The final atomic parameters are reported in Table 2 with their standard deviations. Table 3 gives the full list of observed and calculated squared structure factors. Fig. 2 shows a perspective representation of the atomic thermal ellipsoids.

Discussion of the structure

The mode of coordination around the metal atom is

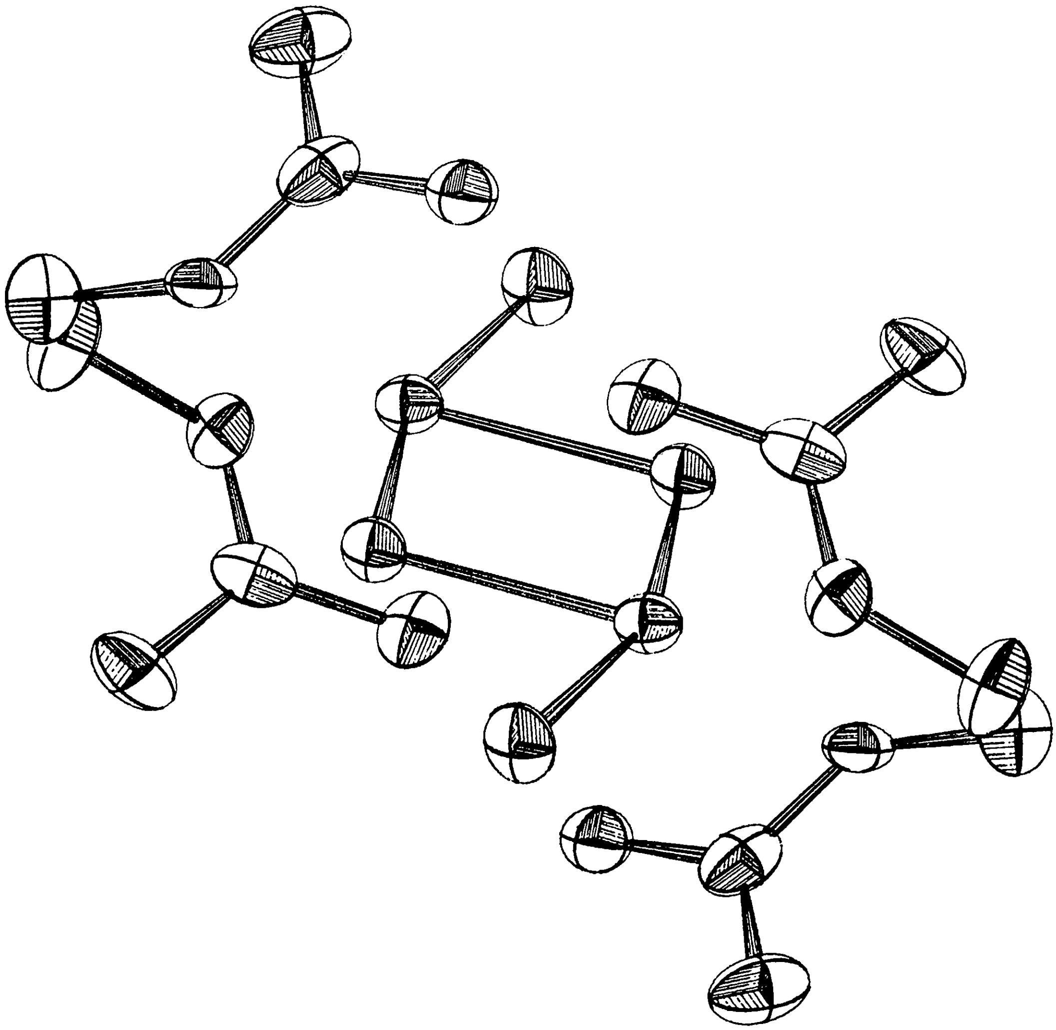


Fig. 2. Perspective representation of the atomic thermal ellipsoids, in the same projection as Fig. 1.

Table 3. *Comparison between the observed and calculated squared structure factors*

An asterisk stands for 'less than'.

H	K	L	$\lvert F_O\rvert^2$	$\lvert F_C\rvert^2$
0	0	0	******	94464
2	0	0	4422	4960
3	0	0	202	270
4	0	0	386	380
5	0	0	1632	1884
6	0	0	1673	1927
7	0	0	121	64
8	0	0	773	896
9	0	0	824	936
10	0	0	*12	26
11	0	0	176	193
12	0	0	*14	7
13	0	0	90	76
2	1	0	1209	1232
3	1	0	557	380
4	1	0	2940	2900
5	1	0	4003	4902
6	1	0	25	90
7	1	0	1267	1225
8	1	0	734	724
9	1	0	66	49
10	1	0	400	357
11	1	0	79	81
12	1	0	119	142
13	1	0	236	139
-2	1	0	90	100
-3	1	0	342	119
-4	1	0	1681	1722
-5	1	0	496	420
-6	1	0	2985	3136
-7	1	0	442	416
-8	1	0	290	331
-9	1	0	486	350
-10	1	0	380	339
-11	1	0	*13	7
-12	1	0	117	106
-13	1	0	*16	6
0	2	0	71	66
1	2	0	40	72
2	2	0	176	132
3	2	0	1529	1253
4	2	0	9860	7645
5	2	0	190	196
6	2	0	1367	1303
7	2	0	335	376
8	2	0	96	62
9	2	0	193	190
10	2	0	331	372
11	2	0	177	190
12	2	0	372	320
-1	2	0	4761	5316
-2	2	0	1482	1092
-3	2	0	79	42
-4	2	0	166	146
-5	2	0	3150	3564
-6	2	0	*6	80
-7	2	0	1832	1971
-8	2	0	*8	0
-9	2	0	392	346
-10	2	0	562	442
-11	2	0	199	210
-12	2	0	44	46
-13	2	0	83	112
0	3	0	412	502
1	3	0	310	74
2	3	0	*4	69
3	3	0	3624	4122
4	3	0	2570	2470
5	3	0	1826	888
6	3	0	1050	1069
7	3	0	52	49
8	3	0	69	77
9	3	0	376	386
10	3	0	64	93
11	3	0	530	494
12	3	0	116	58
-1	3	0	*3	5
-2	3	0	8742	9216
-3	3	0	2570	3102
-4	3	0	33	48
-5	3	0	1506	1601
-6	3	0	1513	1459
-7	3	0	240	199
-8	3	0	724	586
-9	3	0	*11	21
-10	3	0	233	219
-11	3	0	731	706
-12	3	0	106	92
-13	3	0	100	90
0	4	0	605	557
1	4	0	346	357
2	4	0	2927	3083
3	4	0	3069	3024
4	4	0	369	369
5	4	0	1513	1332
6	4	0	*0	3
7	4	0	77	66
8	4	0	380	392
9	4	0	74	72
10	4	0	513	471
11	4	0	185	199
12	4	0	*17	4
-1	4	0	3472	3226
-2	4	0	289	219
-3	4	0	4626	5027
-4	4	0	906	1050
-5	4	0	31	31
-6	4	0	1176	1296
-7	4	0	882	847
-8	4	0	204	112
-9	4	0	480	392
-10	4	0	*12	16
-11	4	0	282	188
-12	4	0	428	250
-13	4	0	*17	12
0	5	0	1063	773
1	5	0	3387	3069
2	5	0	2632	2470
3	5	0	*7	1
4	5	0	1063	1063
5	5	0	*8	5
6	5	0	204	204
7	5	0	282	256
8	5	0	234	243
9	5	0	310	331
10	5	0	376	408
11	5	0	*16	2
-1	5	0	1608	1391
-2	5	0	2294	1806
-3	5	0	676	524
-4	5	0	1632	1391
-5	5	0	159	112
-6	5	0	168	90
-7	5	0	936	981
-8	5	0	471	480
-9	5	0	137	92
-10	5	0	154	121
-11	5	0	72	9
-12	5	0	96	90
0	6	0	1632	1475
1	6	0	1616	1452
2	6	0	412	408
3	6	0	918	870
4	6	0	296	324
5	6	0	426	380
6	6	0	361	357
7	6	0	164	164
8	6	0	132	135
9	6	0	353	376
10	6	0	*16	4
-1	6	0	339	303
-2	6	0	930	864
-3	6	0	386	329
-4	6	0	586	454
-5	6	0	900	858
-6	6	0	46	48
-7	6	0	400	384
-8	6	0	876	840
-9	6	0	62	55
-10	6	0	69	86
-11	6	0	*15	28
-12	6	0	*17	7
0	7	0	1037	912
1	7	0	269	250
2	7	0	445	380
3	7	0	543	403
4	7	0	296	279
5	7	0	600	540
6	7	0	310	303
7	7	0	*14	3
8	7	0	445	404
9	7	0	*16	10
-1	7	0	790	786
-2	7	0	*8	22
-3	7	0	896	829
-4	7	0	243	156
-5	7	0	185	161
-6	7	0	480	404
-7	7	0	58	46
-8	7	0	313	266
-9	7	0	586	480
-10	7	0	*15	3
-11	7	0	114	98
0	8	0	151	144
1	8	0	94	92
2	8	0	210	213
3	8	0	146	174
4	8	0	543	511
5	8	0	272	279
6	8	0	*14	23
7	8	0	376	320
8	8	0	*16	77
-1	8	0	824	807
-2	8	0	462	565
-3	8	0	154	191
-4	8	0	645	520
-5	8	0	102	90
-6	8	0	59	59
-7	8	0	174	159
-8	8	0	*14	1
-9	8	0	324	225
-10	8	0	174	196
-11	8	0	*10	8
0	9	0	*12	4
1	9	0	331	317
2	9	0	*13	9
3	9	0	462	442
4	9	0	110	123
5	9	0	*14	10
6	9	0	79	44
7	9	0	100	86
-1	9	0	240	243
-2	9	0	497	380
-3	9	0	119	104
-4	9	0	100	90
-5	9	0	404	376
-6	9	0	*14	23
-7	9	0	199	150
-8	9	0	106	58
-9	9	0	*16	25
-10	9	0	*18	186
0	10	0	279	276
1	10	0	*14	32
2	10	0	286	276
3	10	0	207	210
4	10	0	*16	29
5	10	0	*17	6
-1	10	0	*14	10
-2	10	0	125	114
-3	10	0	303	272
-4	10	0	*14	25
-5	10	0	246	236
-6	10	0	210	253
-7	10	0	*16	2
-8	10	0	*17	64
0	11	0	*15	10
1	11	0	96	125
2	11	0	292	269
3	11	0	*17	67
-1	11	0	130	114
-2	11	0	*16	29
-3	11	0	*16	55
-4	11	0	176	199
-5	11	0	*17	0
-6	11	0	337	169
2	0	1	740	745
3	0	1	5308	6480
4	0	1	5373	4998
5	0	1	384	339
6	0	1	1197	1122
7	0	1	69	64
8	0	1	645	615
9	0	1	1806	1592
10	0	1	144	96
11	0	1	486	447
12	0	1	*23	11
13	0	1	*26	4
-1	0	1	253	299
-2	0	1	973	1608
-3	0	1	231	353
-4	0	1	437	384
-5	0	1	2144	2798
-6	0	1	2798	3636
-7	0	1	*12	26
-8	0	1	924	1109
-9	0	1	*17	35
-10	0	1	*19	36
-11	0	1	154	193
-12	0	1	*25	17
-13	0	1	154	164
0	1	1	2601	2643
1	1	1	293	219
2	1	1	4238	4469
3	1	1	7006	6225
4	1	1	902	438
5	1	1	3906	3600
6	1	1	154	164
7	1	1	818	685
8	1	1	1170	1011
9	1	1	681	681
10	1	1	342	331
11	1	1	219	219
-1	1	1	5806	6225
-2	1	1	1032	1482
-3	1	1	1714	1697
-4	1	1	801	906
-5	1	1	562	650
-6	1	1	2421	2591
-7	1	1	790	835
-8	1	1	154	234
-9	1	1	194	176
-10	1	1	*19	4
-11	1	1	*23	10
-12	1	1	136	164
-13	1	1	*29	2
0	2	1	426	185
1	2	1	2181	1149
-1	2	1	9702	6790
0	3	1	1626	1183
1	3	1	471	511
-1	3	1	156	86
0	4	1	1714	1203
1	4	1	353	493
-1	4	1	434	486
0	5	1	166	146
1	5	1	1340	1232
-1	5	1	412	386
0	6	1	390	376
1	6	1	2237	2352
-1	6	1	37	37
0	7	1	1971	1962
1	7	1	286	246
-1	7	1	206	220
0	8	1	486	588
1	8	1	159	159
-1	8	1	713	775
0	9	1	*12	4
1	9	1	331	289
-1	9	1	488	442
0	10	1	100	161
1	10	1	72	41
-1	10	1	*18	11
0	11	1	*16	36
1	11	1	*22	42
-1	11	1	83	110
3	-1	1	202	206
4	-1	1	4650	3896
5	-1	1	2400	2209
6	-1	1	756	876
7	-1	1	441	437
8	-1	1	85	86
9	-1	1	655	620
10	-1	1	1058	924
11	-1	1	*21	7
12	-1	1	246	142
13	-1	1	*27	6
-2	-1	1	467	538
-3	-1	1	1482	1109
-4	-1	1	1945	1875
-5	-1	1	4356	3733
-6	-1	1	42	36
-7	-1	1	2268	2007
-8	-1	1	76	77
-9	-1	1	202	282
-10	-1	1	228	303
-11	-1	1	*24	83
-12	-1	1	*27	114
0	-2	1	1182	1267
1	-2	1	3516	3306
-1	-2	1	9082	9625
0	-3	1	7140	8064
1	-3	1	14	25
-1	-3	1	49	8
0	-4	1	640	640
1	-4	1	8299	7208
-1	-4	1	2144	1866
0	-5	1	1486	1421
1	-5	1	1544	1626
-1	-5	1	1560	1566
0	-6	1	942	882
1	-6	1	586	635
-1	-6	1	372	388
0	-7	1	164	159
1	-7	1	745	888
-1	-7	1	41	23
0	-8	1	49	46
1	-8	1	262	328
-1	-8	1	353	339
0	-9	1	177	177
1	-9	1	*15	5
-1	-9	1	246	272
0	-10	1	331	342
1	-10	1	151	156
-1	-10	1	*10	23
0	-11	1	*14	22
1	-11	1	176	154
-1	-11	1	128	117
0	-12	1	*16	30
1	-12	1	*22	10
0	0	2	599	697
1	0	2	196	320
2	0	2	110	137
3	0	2	10548	11960
4	0	2	5388	5613
5	0	2	*8	26
6	0	2	310	256
7	0	2	456	361
8	0	2	159	154
9	0	2	1260	1246
10	0	2	*18	55
11	0	2	408	376
12	0	2	412	303
13	0	2	*26	42
-1	0	2	501	449
-2	0	2	7517	10363
-3	0	2	1303	1282
-4	0	2	2025	2798
-5	0	2	1840	2256
-6	0	2	801	900
-7	0	2	96	102
-8	0	2	386	304
-9	0	2	*18	42
-10	0	2	243	240
-11	0	2	207	182
-12	0	2	*26	12
0	1	2	21	29
1	1	2	2562	1422
2	1	2	6194	5506
3	1	2	12144	11570
4	1	2	96	36
5	1	2	1399	1349
6	1	2	243	219
7	1	2	188	246
8	1	2	1225	1149
9	1	2	172	137
10	1	2	135	166
11	1	2	250	262
12	1	2	94	110
13	1	2	*29	20
-1	1	2	1624	1600
-2	1	2	186	199
-3	1	2	3610	6432
-4	1	2	*9	6
-5	1	2	615	626
-6	1	2	912	1049
-7	1	2	410	628
-8	1	2	146	207
-9	1	2	142	142
-10	1	2	186	92
-11	1	2	123	185
-12	1	2	137	86
0	2	2	1136	773
1	2	2	2575	1961
-1	2	2	3721	2488
0	3	2	1018	773
1	3	2	9025	6872
-1	3	2	199	196
0	4	2	3329	2784
1	4	2	1329	1376
-1	4	2	46	69
0	5	2	1318	1089
1	5	2	142	142
-1	5	2	426	486
0	6	2	36	48
1	6	2	1116	1267
-1	6	2	847	1011
0	7	2	1176	1142
1	7	2	296	486
-1	7	2	*13	6
0	8	2	279	290
1	8	2	117	121
-1	8	2	342	392
0	9	2	*13	11
1	9	2	219	253
-1	9	2	196	222
0	10	2	86	135
1	10	2	77	66
-1	10	2	*20	20
0	11	2	81	130
-1	11	2	*22	59
0	-1	2	132	62
1	-1	2	548	471
2	-1	2	2061	2314
3	-1	2	697	562
4	-1	2	7656	7327
5	-1	2	729	610
6	-1	2	*10	3
7	-1	2	202	243
8	-1	2	630	702
9	-1	2	357	292
10	-1	2	1082	1056
11	-1	2	*21	4
12	-1	2	416	320
13	-1	2	166	121
-1	-1	2	8299	7465
-2	-1	2	3293	3276
-3	-1	2	3204	2190
-4	-1	2	2927	2172
-5	-1	2	729	745
-6	-1	2	76	96
-7	-1	2	1246	1210
-8	-1	2	*17	3
-9	-1	2	671	697
-10	-1	2	324	269
-11	-1	2	*24	34
-12	-1	2	*27	48
0	-2	2	2642	3422
1	-2	2	37	44
-1	-2	2	8317	7318
0	-3	2	5761	7639
1	-3	2	3840	3364
-1	-3	2	112	64
0	-4	2	353	346
1	-4	2	6896	6432
-1	-4	2	2430	1910
0	-5	2	676	751
1	-5	2	1739	1998
-1	-5	2	1739	1772
0	-6	2	1163	1260
1	-6	2	*8	12
-1	-6	2	*10	1
0	-7	2	133	98
1	-7	2	428	449
-1	-7	2	437	388
0	-8	2	428	581
1	-8	2	61	55
-1	-8	2	745	740
0	-9	2	460	557
1	-9	2	361	396
-1	-9	2	135	120
0	-10	2	204	228
1	-10	2	467	494
-1	-10	2	*10	1
0	-11	2	*14	10
1	-11	2	193	188
-1	-11	2	102	67
0	-12	2	*16	20
1	-12	2	*22	4
-1	-12	2	*22	50
0	0	3	98	26
1	0	3	243	441
2	0	3	449	372
3	0	3	4597	4330
4	0	3	3782	3329
5	0	3	*9	3
6	0	3	1018	858
7	0	3	2372	2352
8	0	3	*14	1
9	0	3	773	605
10	0	3	*18	12
11	0	3	*21	71
12	0	3	571	431
13	0	3	286	259
-1	0	3	1246	1325
-2	0	3	4802	8237
-3	0	3	1005	1043
-4	0	3	1089	1391
-5	0	3	562	635
-6	0	3	*13	6
-7	0	3	177	172
-8	0	3	272	279
-9	0	3	*19	45
-10	0	3	392	337
-11	0	3	*25	79
-12	0	3	*27	1
0	1	3	449	426
1	1	3	445	562
2	1	3	1918	1362
3	1	3	4096	3469
4	1	3	324	37
5	1	3	156	144
6	1	3	1806	2025
7	1	3	449	376
8	1	3	1347	1274
9	1	3	*18	30
10	1	3	218	231
11	1	3	196	290
12	1	3	269	376
13	1	3	*29	18
-1	1	3	*6	4
-2	1	3	2125	2043
-3	1	3	3622	4083
-4	1	3	154	193
-5	1	3	671	847
-6	1	3	313	372
-7	1	3	*16	14
-8	1	3	317	350
-9	1	3	117	182
-10	1	3	159	185
-11	1	3	164	193
-12	1	3	*29	17
0	2	3	1521	942
1	2	3	1340	1163
-1	2	3	1584	1274
0	3	3	346	193
1	3	3	11867	7656
-1	3	3	364	412
0	4	3	3102	2591
1	4	3	2756	2218
-1	4	3	*10	4
0	5	3	1482	1289
1	5	3	*10	10
-1	5	3	762	826
0	6	3	151	144
1	6	3	169	155
-1	6	3	1731	1665
0	7	3	493	424
1	7	3	149	149
-1	7	3	72	86
0	8	3	108	144
1	8	3	*10	25
-1	8	3	166	176
0	9	3	*14	4
1	9	3	169	213
-1	9	3	121	125
0	10	3	*16	42
1	10	3	137	166
-1	10	3	*22	14
0	-1	3	2411	2352
1	-1	3	90	166
2	-1	3	6626	5837
3	-1	3	*6	1
4	-1	3	5898	6320
5	-1	3	756	630
6	-1	3	*10	48
7	-1	3	767	826
8	-1	3	1697	1665
9	-1	3	*17	32
10	-1	3	346	272
11	-1	3	*21	4
12	-1	3	*24	64
13	-1	3	404	396
-1	-1	3	5640	5013
-2	-1	3	1608	1334
-3	-1	3	1462	1246
-4	-1	3	729	686
-5	-1	3	76	52
-6	-1	3	188	185
-7	-1	3	704	810
-8	-1	3	*18	20
-9	-1	3	655	676
-10	-1	3	202	172
-11	-1	3	*26	5
0	-2	3	1781	2959
1	-2	3	1673	2043
-1	-2	3	4496	4720
0	-3	3	4045	5205
1	-3	3	1452	1681
-1	-3	3	1918	1136
0	-4	3	630	605
1	-4	3	1011	1163
-1	-4	3	2401	2067
0	-5	3	882	835
1	-5	3	256	269
-1	-5	3	605	595
0	-6	3	1156	1232
1	-6	3	112	161
-1	-6	3	1043	926
0	-7	3	32	46
1	-7	3	973	1089
-1	-7	3	1376	1260
0	-8	3	801	896
1	-8	3	169	193
-1	-8	3	1282	1267
0	-9	3	576	692
1	-9	3	361	462
-1	-9	3	*15	22
0	-10	3	*12	32
1	-10	3	292	339
-1	-10	3	66	49
0	-11	3	*14	16
1	-11	3	121	117
-1	-11	3	76	35
0	-12	3	55	56
1	-12	3	*22	7
-1	-12	3	*22	12
0	0	4	139	125
1	0	4	3272	3612
2	0	4	640	562
3	0	4	829	562
4	0	4	484	404
5	0	4	151	96
6	0	4	1456	1513
7	0	4	3422	3034
8	0	4	76	76
9	0	4	253	164
10	0	4	86	58
11	0	4	*22	6
12	0	4	313	250
13	0	4	210	190
-1	0	4	1075	1858
-2	0	4	1436	1600
-3	0	4	552	590
-4	0	4	632	650
-5	0	4	185	210
-6	0	4	502	543
-7	0	4	404	441
-8	0	4	*19	90
-9	0	4	*22	10
-10	0	4	216	142
-11	0	4	*27	15
0	1	4	3080	2852
1	1	4	1962	2401
2	1	4	961	708
3	1	4	590	428
4	1	4	*11	13
5	1	4	338	292
6	1	4	2200	2172
7	1	4	441	428
8	1	4	120	135
9	1	4	71	104
10	1	4	*21	8
11	1	4	164	228
12	1	4	210	292
13	1	4	*29	16
-1	1	4	1369	1096
-2	1	4	1756	1786
-3	1	4	906	900
-4	1	4	*14	18
-5	1	4	586	625
-6	1	4	*16	1
-7	1	4	269	388
-8	1	4	253	279
-9	1	4	142	90
-10	1	4	96	98
-11	1	4	*29	123
0	2	4	3564	2643
1	2	4	49	149
-1	2	4	671	530
0	3	4	*6	9
1	3	4	1063	1467
-1	3	4	1211	926
0	4	4	1640	1289
1	4	4	237	320
-1	4	4	*12	0
0	5	4	918	795
1	5	4	*12	1
-1	5	4	1011	942
0	6	4	188	137
1	6	4	193	156
-1	6	4	1584	1537
0	7	4	96	86
1	7	4	240	262
-1	7	4	166	222
0	8	4	96	86
1	8	4	*16	72
-1	8	4	*10	6
0	9	4	*15	16
1	9	4	*21	23
-1	9	4	79	64
0	-1	4	1681	1910
1	-1	4	236	236
2	-1	4	5170	5135
3	-1	4	441	412
4	-1	4	182	228
5	-1	4	751	807
6	-1	4	276	306
7	-1	4	1689	1079
8	-1	4	1918	2228
9	-1	4	*17	0
10	-1	4	146	151
11	-1	4	110	123
12	-1	4	*24	1
13	-1	4	342	246
-1	-1	4	1436	1340
-2	-1	4	655	520
-3	-1	4	449	441
-4	-1	4	1190	930
-5	-1	4	154	166
-6	-1	4	1122	1030
-7	-1	4	416	408
-8	-1	4	*19	0
-9	-1	4	225	237
-10	-1	4	*26	22
-11	-1	4	*29	61
0	-2	4	961	1340
1	-2	4	1260	1537
-1	-2	4	372	326
0	-3	4	961	1005
1	-3	4	1482	1681
-1	-3	4	185	210
0	-4	4	320	316
1	-4	4	156	239
-1	-4	4	2450	1989
0	-5	4	801	882
1	-5	4	412	441
-1	-5	4	416	337
0	-6	4	376	428
1	-6	4	529	702
-1	-6	4	119	142
0	-7	4	34	23
1	-7	4	751	967
-1	-7	4	713	751
0	-8	4	676	655
1	-8	4	132	130
-1	-8	4	676	635
0	-9	4	384	400
1	-9	4	286	286
-1	-9	4	196	96
0	-10	4	*13	17
1	-10	4	181	151
-1	-10	4	225	264
0	-11	4	112	137
1	-11	4	72	56
-1	-11	4	104	46
0	-12	4	112	108
1	-12	4	110	81
0	0	5	*6	1
1	0	5	2490	2725
2	0	5	1956	1681
3	0	5	289	213
4	0	5	437	335
5	0	5	942	896
6	0	5	1232	1082
7	0	5	2079	1875
8	0	5	*16	22
9	0	5	110	53
10	0	5	676	590
11	0	5	137	164
12	0	5	137	112
13	0	5	*27	16
-1	0	5	818	767
-2	0	5	128	112
-3	0	5	*13	3
-4	0	5	424	424
-5	0	5	125	159
-6	0	5	471	557
-7	0	5	342	339
-8	0	5	*22	17
-9	0	5	*23	3
-10	0	5	*26	50
0	1	5	1832	1467
1	1	5	1927	2061
2	1	5	154	139
3	1	5	*12	6
4	1	5	681	681
5	1	5	65	112
6	1	5	2267	2266
7	1	5	104	117
8	1	5	*18	41
9	1	5	303	350
10	1	5	306	350
11	1	5	182	154
12	1	5	*27	86
-1	1	5	404	292
-2	1	5	416	445
-3	1	5	*14	10
-4	1	5	76	74
-5	1	5	313	365
-6	1	5	*18	0
-7	1	5	279	416
-8	1	5	243	206
-9	1	5	*26	23
-10	1	5	106	55
0	2	5	2852	2052
1	2	5	61	92
-1	2	5	655	404
0	3	5	236	174
1	3	5	137	243
-1	3	5	2694	2144
0	4	5	458	380
1	4	5	110	149
-1	4	5	445	384
0	5	5	464	346
1	5	5	93	72
0	6	5	137	110
-1	6	5	*17	219
0	7	5	*13	2
1	7	5	272	256
-1	7	5	320	64
0	8	5	74	104
1	8	5	182	204
-1	8	5	*21	0
0	9	5	90	121
1	9	5	*24	3
0	-1	5	1706	1980
1	-1	5	480	449
2	-1	5	3956	3721
3	-1	5	1076	1069
4	-1	5	56	86
5	-1	5	1024	1085
6	-1	5	697	676
7	-1	5	713	801
8	-1	5	784	710
9	-1	5	*18	62
10	-1	5	*21	83
11	-1	5	740	676
12	-1	5	*26	66
13	-1	5	*29	67
-1	-1	5	380	416
-2	-1	5	121	110
-3	-1	5	784	745
-4	-1	5	961	888
-5	-1	5	396	335
-6	-1	5	940	762
-7	-1	5	*19	6
-8	-1	5	*23	1
-9	-1	5	*26	38
-10	-1	5	*27	7
0	-2	5	635	896
1	-2	5	1306	1465
-1	-2	5	1384	1163
0	-3	5	484	511
1	-3	5	1529	1681
-1	-3	5	1544	1190
0	-4	5	1103	1513
1	-4	5	32	26
-1	-4	5	686	666
0	-5	5	702	686
1	-5	5	1601	1066
-1	-5	5	515	576
0	-6	5	303	222
1	-6	5	967	1136
-1	-6	5	*12	14
0	-7	5	*8	3
1	-7	5	262	310
-1	-7	5	320	320
0	-8	5	199	169
1	-8	5	*14	3
-1	-8	5	92	70
0	-9	5	69	46
1	-9	5	98	108
-1	-9	5	164	129
0	-10	5	48	59
1	-10	5	*18	18
-1	-10	5	256	237
0	-11	5	220	204
1	-11	5	*20	3
-1	-11	5	154	130
0	-12	5	130	135
1	-12	5	112	121
0	0	6	48	49
1	0	6	1136	1362
2	0	6	961	745
3	0	6	562	441
4	0	6	538	304
5	0	6	1354	1325
6	0	6	*15	9
7	0	6	328	282
8	0	6	*16	108
9	0	6	*19	7
10	0	6	1005	1005
11	0	6	376	350
12	0	6	*26	38
-1	0	6	812	835
-2	0	6	*14	0
-3	0	6	640	610
-4	0	6	456	392
-5	0	6	*18	28
-6	0	6	151	139
-7	0	6	161	142
-8	0	6	*25	2
-9	0	6	*26	45
0	1	6	1190	942
1	1	6	708	824
2	1	6	420	249
3	1	6	74	79
4	1	6	1176	1076
5	1	6	*16	12
6	1	6	234	324
7	1	6	71	71
8	1	6	*19	1
9	1	6	552	420
10	1	6	446	420
11	1	6	*27	14
12	1	6	*29	40
-1	1	6	128	92
-2	1	6	641	428
-3	1	6	108	202
-4	1	6	440	497
-5	1	6	149	225
-6	1	6	*21	7
-7	1	6	149	287
-8	1	6	*26	90
-9	1	6	*29	26
0	2	6	1332	835
1	2	6	361	666
-1	2	6	262	185
0	3	6	1043	773
1	3	6	*13	66
-1	3	6	1043	949
0	4	6	37	31
1	4	6	128	199
-1	4	6	357	486
0	5	6	59	67
1	5	6	144	210
-1	5	6	*17	15
0	6	6	65	62
-1	6	6	*18	13
0	7	6	*14	4
-1	7	6	*21	34
0	8	6	74	82
-1	8	6	*26	18
0	-1	6	961	1063
1	-1	6	*10	26
2	-1	6	600	586
3	-1	6	930	1096
4	-1	6	339	449
5	-1	6	1421	1504
6	-1	6	1116	1211
7	-1	6	*17	46
8	-1	6	69	72
9	-1	6	106	135
10	-1	6	85	53
11	-1	6	681	818
12	-1	6	*27	62
13	-1	6	*31	20
-1	-1	6	164	172
-2	-1	6	740	615
-3	-1	6	1204	1076
-4	-1	6	233	222
-5	-1	6	71	121
-6	-1	6	186	169
-7	-1	6	*23	2
-8	-1	6	*26	61
-9	-1	6	*27	41
0	-2	6	*7	[illegible]
1	-2	6	999	1267
-1	-2	6	1332	1310
0	-3	6	747	1063
1	-3	6	269	396
-1	-3	6	1056	967
0	-4	6	1030	1444
1	-4	6	*10	5
-1	-4	6	488	526
0	-5	6	835	1063
1	-5	6	1156	1347
-1	-5	6	45	52
0	-6	6	*8	3
1	-6	6	660	826
-1	-6	6	132	182
0	-7	6	176	169
1	-7	6	*13	4
-1	-7	6	72	31
0	-8	6	*11	31
1	-8	6	151	144
-1	-8	6	*17	2
0	-9	6	*32	17
1	-9	6	106	96
-1	-9	6	136	96
0	-10	6	*14	14
1	-10	6	*10	1
-1	-10	6	269	220
0	-11	6	106	116
1	-11	6	*21	14
-1	-11	6	110	76
0	0	7	269	206
1	0	7	*12	18
2	0	7	918	756
3	0	7	310	279
4	0	7	1050	968
5	0	7	1182	1050
6	0	7	98	161
7	0	7	*10	2
8	0	7	206	225
9	0	7	*22	1
10	0	7	400	416
11	0	7	144	85
12	0	7	*29	1
-1	0	7	437	462
-2	0	7	*17	59
-3	0	7	756	466
-4	0	7	77	77
-5	0	7	*21	16
-6	0	7	*23	13
-7	0	7	125	49
-8	0	7	*27	46
0	1	7	*10	3
1	1	7	213	213
2	1	7	467	420
3	1	7	240	317
4	1	7	1414	1362
5	1	7	182	188
6	1	7	*19	4
7	1	7	182	190
8	1	7	85	32
9	1	7	546	576
10	1	7	262	231
11	1	7	*26	1
-1	1	7	149	144
-2	1	7	188	219
-3	1	7	125	130
-4	1	7	534	437
-5	1	7	85	117
-6	1	7	*26	1
-7	1	7	*27	69
-8	1	7	*29	1
0	2	7	106	85
1	2	7	196	304
-1	2	7	*15	25
0	3	7	420	296
1	3	7	*15	77
-1	3	7	331	231
0	4	7	89	112
1	4	7	128	219
-1	4	7	219	222
0	5	7	*14	34
1	5	7	216	426
-1	5	7	90	88
0	6	7	119	110
-1	6	7	*21	6
0	7	7	*17	16
0	-1	7	887	718
1	-1	7	177	243
2	-1	7	*16	3
3	-1	7	756	751
4	-1	7	61	114
5	-1	7	942	967
6	-1	7	882	778
7	-1	7	104	125
8	-1	7	*21	25
9	-1	7	193	228
10	-1	7	*24	15
11	-1	7	196	206
12	-1	7	*29	30
-1	-1	7	154	156
-2	-1	7	1063	908
-3	-1	7	548	426
-4	-1	7	*19	5
-5	-1	7	*21	13
-6	-1	7	88	66
-7	-1	7	*26	13
-8	-1	7	174	161
0	-2	7	342	310
1	-2	7	219	331
-1	-2	7	400	400
0	-3	7	44	53
1	-3	7	104	132
-1	-3	7	773	847
0	-4	7	756	716
1	-4	7	*12	14
-1	-4	7	49	56
0	-5	7	310	289
1	-5	7	581	492
-1	-5	7	272	289
0	-6	7	219	177
1	-6	7	304	296
-1	-6	7	353	313
0	-7	7	520	426
1	-7	7	76	100
-1	-7	7	102	67
0	-8	7	144	110
1	-8	7	282	342
-1	-8	7	*10	4
0	-9	7	*14	6
1	-9	7	199	204
-1	-9	7	144	182
0	-10	7	*14	25
1	-10	7	*20	12
-1	-10	7	79	46
0	-11	7	*16	26
1	-11	7	*22	14
0	0	8	396	342
1	0	8	250	249
2	0	8	280	193
3	0	8	276	199
4	0	8	353	249
5	0	8	369	289
6	0	8	384	380
7	0	8	*22	26
8	0	8	497	581
9	0	8	*21	40
10	0	8	104	76
11	0	8	*29	7
-1	0	8	102	100
-2	0	8	21	1
-3	0	8	233	231
-4	0	8	90	99
-5	0	8	*25	14
-6	0	8	*26	50
0	1	8	182	190
1	1	8	59	31
2	1	8	303	313
3	1	8	154	166
4	1	8	576	600
5	1	8	164	237
6	1	8	*23	50
7	1	8	296	246
8	1	8	159	188
9	1	8	*27	61
10	1	8	*29	36
-1	1	8	262	256
-2	1	8	193	216
-3	1	8	*24	22
-4	1	8	243	253
-5	1	8	*24	12
-6	1	8	*29	36
0	2	8	55	17
1	2	8	188	276
-1	2	8	110	49
0	3	8	287	135
1	3	8	*18	5
-1	3	8	*18	4
0	4	8	64	40
1	4	8	76	98
-1	4	8	106	64
0	5	8	*16	37
1	5	8	137	216
-1	5	8	137	77
0	-1	8	339	296
1	-1	8	420	515
2	-1	8	159	191
3	-1	8	462	372
4	-1	8	71	79
5	-1	8	100	132
6	-1	8	253	210
7	-1	8	296	396
8	-1	8	*23	117
9	-1	8	552	576
10	-1	8	*27	1
11	-1	8	*29	12
-1	-1	8	56	32
-2	-1	8	180	222
-3	-1	8	81	39
-4	-1	8	*24	42
-5	-1	8	*26	94
-6	-1	8	*27	31
0	-2	8	164	172
1	-2	8	303	392
-1	-2	8	262	196
0	-3	8	52	44
1	-3	8	71	108
-1	-3	8	303	272
0	-4	8	228	180
1	-4	8	*14	0
-1	-4	8	*15	2
0	-5	8	*12	23
1	-5	8	92	96
-1	-5	8	428	480
0	-6	8	228	193
1	-6	8	*15	128
-1	-6	8	901	862
0	-7	8	670	530
1	-7	8	106	89
-1	-7	8	67	41
0	-8	8	156	119
1	-8	8	384	416
-1	-8	8	*20	40
0	-9	8	*14	18
1	-9	8	246	250
-1	-9	8	79	35
0	-10	8	85	53
1	-10	8	*21	1
-1	-10	8	*22	8
0	0	9	447	386
1	0	9	199	219
2	0	9	110	86
3	0	9	185	166
4	0	9	*22	3
5	0	9	*23	42
6	0	9	185	166
7	0	9	*25	15
8	0	9	306	386
9	0	9	137	96
-1	0	9	*18	20
-2	0	9	*23	6
-3	0	9	*25	71
-4	0	9	*26	2
0	1	9	299	246
1	1	9	*10	9
2	1	9	180	180
3	1	9	*26	20
4	1	9	*26	44
5	1	9	219	279
6	1	9	*26	1
7	1	9	902	412
8	1	9	142	138
9	1	9	*31	6
-1	1	9	303	231
-2	1	9	96	40
-3	1	9	*27	4
-4	1	9	*29	59
0	2	9	*14	9
1	2	9	90	166
-1	2	9	220	136
0	3	9	100	85
1	3	9	*21	8
-1	3	9	*22	9
0	4	9	*17	30
1	4	9	85	50
0	-1	9	92	64
1	-1	9	392	457
2	-1	9	*25	16
3	-1	9	219	253
4	-1	9	*23	76
5	-1	9	*23	9
6	-1	9	*26	16
7	-1	9	*26	100
8	-1	9	*26	39
9	-1	9	276	320
10	-1	9	*29	76
-1	-1	9	*18	16
-2	-1	9	*24	32
-3	-1	9	*26	8
-4	-1	9	139	125
0	-2	9	*12	5
1	-2	9	166	222
-1	-2	9	*18	29
0	-3	9	74	41
1	-3	9	*17	15
-1	-3	9	*18	14
0	-4	9	*12	22
1	-4	9	*17	106
-1	-4	9	*18	5
0	-5	9	*13	2
1	-5	9	*18	61
-1	-5	9	388	331
0	-6	9	222	172
1	-6	9	*18	5
-1	-6	9	339	283
0	-7	9	262	182
1	-7	9	*18	27
-1	-7	9	*20	5
0	-8	9	*15	22
1	-8	9	182	128
-1	-8	9	*21	11
0	-9	9	64	36
1	-9	9	*21	36
0	0	10	207	125
1	0	10	104	45
2	0	10	*26	56
3	0	10	102	44
4	0	10	228	196
5	0	10	*26	1
6	0	10	105	128
7	0	10	27	24
-1	0	10	83	2
-2	0	10	*27	30
0	1	10	154	90
1	1	10	137	44
2	1	10	106	85
3	1	10	123	96
4	1	10	106	46
5	1	10	146	85
6	1	10	*29	4
-1	1	10	139	100
0	2	10	*17	5
1	2	10	*22	137
0	-1	10	*14	7
1	-1	10	142	142
2	-1	10	*26	4
3	-1	10	96	96
4	-1	10	146	105
5	-1	10	135	164
6	-1	10	*27	62
7	-1	10	*29	62
8	-1	10	*29	55
-1	-1	10	132	62
-2	-1	10	*29	11
0	-2	10	114	119
1	-2	10	*20	12
-1	-2	10	77	27
0	-3	10	114	119
1	-3	10	121	112
-1	-3	10	*21	7
0	-4	10	*14	10
1	-4	10	149	262
1	-4	10	*21	5
0	-5	10	*14	21
1	-5	10	*20	45
-1	-5	10	79	42
0	-6	10	61	32
1	-6	10	*21	15
-1	-6	10	*22	12
0	-7	10	*16	6
1	-7	10	*21	13
-1	-7	10	*22	0
1	-8	10	*22	6
0	-2	11	114	106
0	-3	11	177	125
0	-4	11	*17	

represented in Fig. 3. The resulting geometry is best described in terms of a slightly distorted trigonal bipyramid, provided we idealize each allyl group as a monodentate ligand, bonded to the metal through the centre of mass of the three allyl C atoms. In fact, the centres of the two allyl groups at the left- and right-hand side in Fig. 3 are only displaced by −0·07 and +0·17 Å with respect to the horizontal plane crossing the Ru atom; the corresponding displacement of the Cl(2) atom is −0·20 Å. The bond angles between the equatorial substituents are very close to 120°. The straight line joining the two apical chlorine atoms, Cl(1) and Cl(2′), is only 0·42 Å away from the metal atom, the distortion occurring toward the gap of the organic ligand, as in the case of $RuCl_2C_{12}H_{18}$ (Lydon & Truter, 1968). The molecular fragment shown in Fig. 3 contains a pseudo-twofold axis connecting the centre of the C(4)–C(5) bond and the ruthenium atom: the greatest atomic displacement from the exact twofold symmetry does not exceed 0·2 Å. The dihedral angles defined by the equatorial plane of Fig. 3 and the planes of the allyl groups are 65·4 and 63·3° for C(1)–C(2)–C(3) and C(6)–C(7)–C(8), respectively; the two values are close to the average value (63·2°) reported for $RuCl_2C_{12}H_{18}$ (Lydon & Truter, 1968).

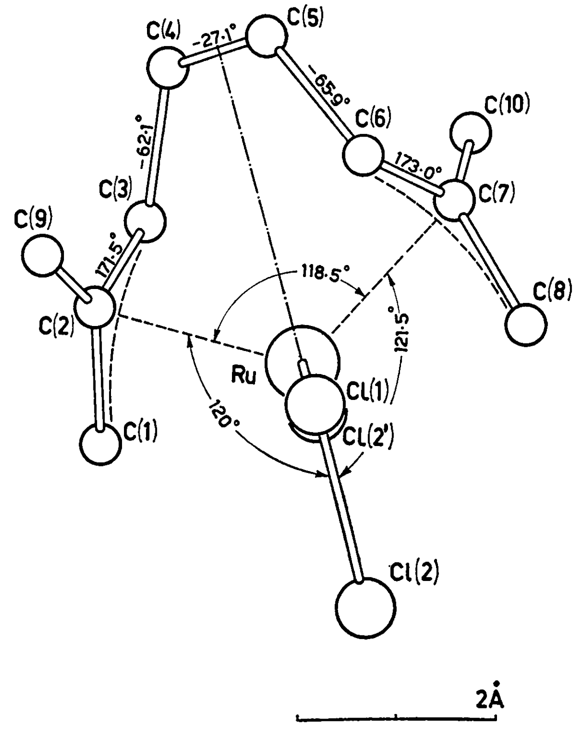


Fig. 3. The geometry of the coordination around the Ru atom is shown. Atoms Cl(2), C(2), C(7) constitute the equatorial vertices of the trigonal bipyramid, Cl(1) and Cl(2′) (overlapping in the figure) its upper and lower vertices. The dihedral angles corresponding to the carbon skeleton of the ligand are indicated (*trans* conformation ≡ 180°). The pseudo-twofold axis is indicated with a dash-and-dot line.

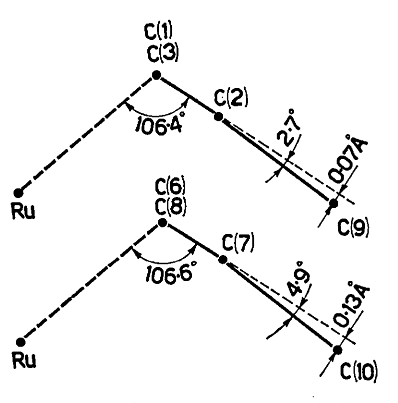


Fig. 4. The two allyl skeletons of the organic ligand seen along vectors C(1)–C(3) and C(6)–C(8).

As shown in Fig. 4, both methyl groups deviate from the allyl plane toward the half space containing the metal atom, in accordance with that reported for other metal complexes containing 2-methylallyl groups (Uttech & Dietrich, 1965; Mason & Russel, 1966; Mason & Wheeler, 1968). However, in contrast to that reported for the other cases, the angle between the $C–CH_3$ bond and the allyl plane is well below 20°. The two methylenic C atoms connected to the allyl groups are also slightly twisted out of the allyl planes, as is indicated by the C(1)–C(2)–C(3)–C(4) and C(5)–C(6)–C(7)–C(8) dihedral angles which deviate appreciably from 180° (see Fig. 3). The dihedral angle between the planes Ru, C(1), C(3) [or Ru, C(6), C(8)] and C(1), C(2), C(3) [or C(6), C(7), C(8)] is 106·4° (106·6°): these values are close, within a few degrees, to those reported for most metal-allyl π-complexes. The C–C bond lengths of the allyl groups do not show significant differences, nor do the Ru–C distances within each allyl group (see Fig. 1). One allyl group is significantly closer to Ru (2·22 Å being the average distance, with $\sigma = 0·012$ Å) than the other group (average distance = 2·27 Å, with the same σ). No explanation of this difference is possible on grounds of chemical bonding; on the other hand, the structure is centrosymmetric, and therefore no anomalous dispersion effect can account for the difference. The best explanation of this fact seems due to the different crystalline environment of the two allyl groups: as expected, the group which is closer to Ru is affected by more severe contacts with an adjacent molecule, consisting of three intermolecular C···C distances shorter than 3·6 Å (3·37, 3·58 and 3·58 Å), while the other group is involved only in one distance in the same range ($d_{C\cdots Cl} = 3·53$ Å). On the whole, the Ru–C distances to coordinated carbon atoms are distributed in the same range as observed for $RuCl_2C_{12}H_{18}$.

As expected, the shortest Ru–Cl bond length (2·39 Å) corresponds to the simply coordinated Cl atom; this distance is remarkably lower than those reported for $RuCl_2C_{12}H_{18}$ (2·44 and 2·48 Å). The two Ru–Cl bridge bonds have different lengths (2·47 and 2·56 Å), the difference being well above the expected random fluctuation ($\sigma_{\text{Ru-Cl}} = 0.007$ Å). We believe that the greater bond length corresponding to the equatorially substituted chlorine atom is to be attributed to a repulsive effect on the Ru–Cl bonding electrons induced by the allylic π-electrons donated to the metal (see Fig. 3). Owing to the geometry of the coordination, the above effect is analogous to the well-known *trans* effect. Contrary to the case of most dimeric complexes containing chlorine bridges, the Ru_2Cl_2 planar four-membered ring deviates appreciably from the perfect square conformation: in addition to the above discussed difference in the Ru–Cl bond lengths, the Cl–Ru–Cl and Ru–Cl–Ru angles are quite different from 90° (75·2° and 104·8° respectively, see Fig. 1).

We express our gratitude to Drs Porri and Vitulli for providing us with the crystalline samples, and for very useful discussions.

References

CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, paper 6, pp. 32–78. Oxford: Pergamon Press.

IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.

LYDON, J. E., NICHOLSON, J. K., SHAW, B. L. & TRUTER, M. R. (1964). *Proc. Chem. Soc.* p. 421.

LYDON, J. E. & TRUTER, M. R. (1968). *J. Chem. Soc. A*, p. 362.

MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.

MASON, R. & RUSSEL, D. R. (1966). *Chem. Commun.* p. 26.

MASON, R. & WHEELER, A. G. (1968). *J. Chem. Soc. A*, p. 2549.

PORRI, L., GALLAZZI, M. C., COLOMBO, A. & ALLEGRA, G. (1965). *Tetrahedron Letters*, 4187.

UTTECH, R. & DIETRICH, H. (1965). *Z. Kristallogr.* **122**, 60.

VAND, V., EILAND, P. E. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303.

Acta Cryst. (1971). **B27**, 1658

The Crystal Structure of 4-Ethylpyridinium Tetrabromoferrate(III)*

BY MARVIN L. HACKERT† AND ROBERT A. JACOBSON

Institute for Atomic Research and Department of Chemistry Iowa State University, Ames, Iowa 50010, *U.S.A.*

(*Received* 1 *July* 1970)

Single-crystals of 4-ethylpyridinium tetrabromoferrate(III) have been prepared and their crystal structure has been determined by three-dimensional X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.7068$ (8), $b = 14.1673$ (11), $c = 13.0414$ (16) Å, $\beta = 84.19$ (1)°, and $Z = 4$. Intensity data were measured using a θ–2θ step scan technique on an automated diffractometer with Mo $K\alpha$ radiation. The structure was solved by superposition and Fourier methods and refined by full-matrix least-squares techniques to a final residual R of 0·061 for the 762 observed reflections used in the analysis. Ring atoms of the cation were refined as a rigid group. The $FeBr_4^-$ tetrahedra are nearly aligned with their threefold axes almost coincident in the **c** direction. Average Fe–Br distance is 2·326 Å (this average becomes 2·347 Å when the interatomic distances are corrected for thermal motion assuming a riding model). The structure is in part stabilized by the presence of a weak N–H---Br hydrogen bond.

Introduction

The crystal-structure study of 4-ethylpyridinium tetrabromoferrate(III) was undertaken after the compound accidentally appeared as a byproduct during a series of investigations of bromo-coordinated antimony compounds in this laboratory. The true composition was determined from the crystal-structure analysis and also by an electron-microprobe analysis of the crystal used in the data collection. We felt it would be of interest to complete the crystal-structure analysis of the tetrabromoferrate(III) compound because of the general instability of iron(III)bromides (Sidgwick, 1950) and the lack of crystal-structure data regarding the $FeBr_4^-$ group.

Experimental

Crystal data

4-Ethylpyridinium tetrabromoferrate(III),
$C_7H_9NHFeBr_4$,
$M = 483.65$, monoclinic $P2_1/c$, $F(000) = 900e$, $Z = 4$,
$a = 7.7068$ (8), $b = 14.1673$ (11), $c = 13.0414$ (16) Å,
$\beta = 84.19(1)°$,
$V = 1416.6$ Å^3, $D_c = 2.27$ g.cm^{-3},
Mo $K\alpha$ ($\lambda = 0.7107$ Å), $\mu = 135.8$ cm^{-1}.

Single crystals of $C_7H_9NHFeBr_4$ were obtained accidentally from contamination introduced into a vessel where the corresponding antimony bromide salt was being prepared. Of the two crystalline forms present, crystals of what later was determined to be the tetra-

---

* Work was performed at the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2777.

† Present address: Department of Biological Sciences, Purdue University, Lafayette, Indiana 47907, U.S.A.