

## The Structure of Tetramethylammonium Carbidohexadecacarbonylhexaruthenate

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**Abstract.**  $[(\text{CH}_3)_4\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ , orthorhombic, *Pnma*,  $a = 10.144$  (4),  $b = 19.416$  (4),  $c = 36.942$  (6) Å,  $Z = 8$ ,  $D_c = 2.217$  Mg m<sup>-3</sup>,  $V = 7275.5$  Å<sup>3</sup>. 3528 independent reflections have been used to refine the structure giving an *R* value of 0.054. The structure consists of two crystallographically non-equivalent  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  anions each having *m* symmetry. The average non-bridged Ru–Ru distance is  $2.90 \pm 0.10$  Å and that of bridged Ru–Ru is  $2.85 \pm 0.02$  Å. The central C atom is octahedrally coordinated to six Ru atoms with Ru–C distances ranging from 2.038–2.053 Å. The structure is isostructural with the Fe analogue.

**Introduction.** The high-yield synthesis of  $[(\text{CH}_3)_4\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$  and its application in model studies of hydrogenation have been discussed by Bradley & Ansell (1979). Intensity data  $0 < 2\theta < 45^\circ$  (Mo *K* $\alpha$ ) were collected with an orange block of dimensions  $0.2 \times 0.2 \times 0.2$  mm in a thin glass tube on an Enraf–Nonius CAD-4\* diffractometer. A variable scan rate ( $4\text{--}20^\circ \text{ min}^{-1}$ ) was used for data collection with fast scans for intense reflections and slower scans for weaker reflections. Owing to computer limitations, the structure determination was carried out with 3528 reflections having  $F > 6\sigma(I)$ . This utilized *F* values based on statistically reliable intensity measurements [usually  $>2.0 - 1.5\sigma(I)$ ] and still resulted in a high ratio of number of reflections/number of parameters of 14:1.  $\psi$  scans indicated that an absorption correction was negligible. The structure was solved using a combination of direct methods, packing considerations, Fourier and least-squares techniques. During the final cycles of refinement the Ru atoms were refined with anisotropic temperature factors and corrected for anomalous dispersion ( $f' = 1.2$  e,  $f'' = +1.1$  e); the non-metal atoms were refined isotropically. The parameters for one anion were varied on alternate cycles with those of the other, and those for the cations were varied on all cycles. The temperature factors of the four

C atoms in the N(2) tetramethylammonium group were held at  $10 \text{ \AA}^2$  because they assumed large positive values in previous cycles. Using a weighting scheme where  $w^{1/2} = 200/F_o$  for  $F_o > 200$ ,  $w^{1/2} = 1$  for  $80 < F_o < 200$ , and  $w = F_o/80$  for  $F_o < 80$ , full-matrix least-squares refinement ceased when  $R = 0.054$ ,  $wR = 0.056$ . Final atomic coordinates are given in Table 1, bond lengths in Table 2.† Fig. 1 gives a stereoscopic view of the packing of the anions and cations in the four asymmetric units of the unit cell, and Fig. 2 illustrates the molecular configuration and atomic-numbering scheme applicable to either anion.

**Discussion.** The compound is isostructural with its iron analogue  $[(\text{CH}_3)_4\text{N}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$  described by Churchill & Wormald (1974). An asymmetric unit of

† Lists of structure factors, thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34902 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

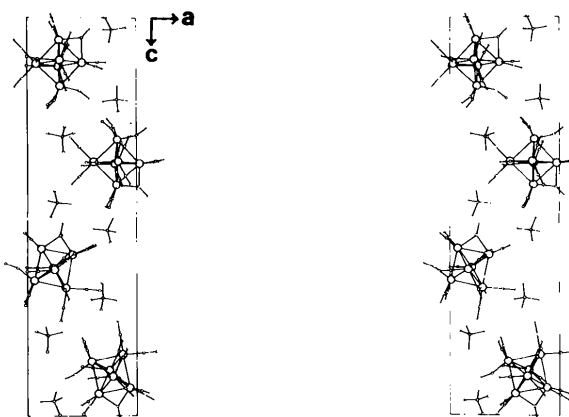


Fig. 1. A stereoscopic view of the contents of a partial unit cell. Anions centered at  $y = \frac{1}{4}$  and cations centered close to  $y = 0$  are shown.

\* The data were collected by Molecular Structures Corporation, College Station, Texas, USA.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ;  $\times 10^5$  for Ru)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
<b>Cluster A</b>				<b>Cluster B</b>			
Ru(1)	27250 (11)	14504 (5)	13136 (3)	Ru(1)	22568 (11)	14513 (6)	62477 (3)
Ru(2)	27402 (16)	25000	7592 (4)	Ru(2)	39038 (15)	25000	59082 (4)
Ru(3)	47763 (15)	25000	12935 (5)	Ru(3)	11640 (16)	25000	57614 (4)
Ru(4)	28192 (17)	25000	18638 (4)	Ru(4)	5666 (16)	25000	65313 (4)
Ru(5)	7429 (15)	25000	13297 (4)	Ru(5)	33040 (16)	25000	67035 (4)
O(1)	-63 (12)	933 (6)	1269 (3)	O(1)	3455 (12)	929 (7)	6936 (3)
O(2)	3663 (12)	511 (7)	729 (3)	O(2)	3859 (14)	397 (8)	5850 (4)
O(3)	3515 (13)	409 (8)	1875 (4)	O(3)	-87 (12)	491 (7)	6271 (3)
O(4)	1916 (14)	1425 (8)	209 (4)	O(4)	5905 (18)	1462 (10)	5675 (5)
O(5)	5525 (18)	2500	471 (5)	O(5)	3067 (20)	2500	5128 (6)
O(6)	6765 (14)	1366 (8)	1369 (4)	O(6)	-277 (16)	1370 (9)	5371 (4)
O(7)	5454 (49)	2500	2166 (12)	O(7)	-1945 (34)	2500	6116 (8)
O(8)	1665 (25)	1442 (13)	2353 (6)	O(8)	-218 (14)	1401 (8)	7071 (4)
O(9)	-1268 (22)	2500	1916 (6)	O(9)	2822 (19)	2500	7505 (6)
O(10)	-1273 (19)	2500	744 (5)	O(10)	6258 (21)	2500	6768 (5)
C(1)	838 (16)	1317 (9)	1295 (4)	C(1)	3119 (16)	1325 (9)	6716 (4)
C(2)	3256 (14)	864 (8)	956 (4)	C(2)	3242 (16)	806 (9)	6014 (4)
C(3)	3164 (15)	812 (8)	1658 (4)	C(3)	853 (16)	843 (9)	6266 (4)
C(4)	2293 (17)	1861 (10)	419 (4)	C(4)	5082 (20)	1872 (11)	5781 (5)
C(5)	4727 (23)	2500	704 (6)	C(5)	2810 (23)	2500	5449 (6)
C(6)	6005 (16)	1827 (9)	1336 (4)	C(6)	285 (18)	1840 (10)	5520 (5)
C(7)	4536 (55)	2500	1972 (14)	C(7)	-900 (38)	2500	6228 (9)
C(8)	2351 (26)	1843 (16)	2165 (7)	C(8)	79 (18)	1839 (10)	6849 (5)
C(9)	-516 (23)	2500	1681 (6)	C(9)	3058 (24)	2500	7177 (6)
C(10)	-510 (23)	2500	969 (6)	C(10)	5110 (24)	2500	6739 (6)
C(11)	2742 (16)	2500	1311 (4)	C(11)	2261 (19)	2500	6225 (5)
<b>N(1) tetramethylammonium cation</b>				<b>N(2) tetramethylammonium cation</b>			
N(1)	8171 (13)	-167 (8)	2031 (4)	N(2)	7370 (14)	-522 (8)	5339 (4)
C(1N1)	6797 (23)	110 (13)	2103 (6)	C(1N2)	8296 (26)	-1147 (14)	5386 (7)
C(2N1)	9207 (23)	415 (14)	2100 (6)	C(2N2)	6020 (25)	-838 (14)	5303 (6)
C(3N1)	8265 (21)	-401 (12)	1644 (6)	C(3N2)	7580 (24)	-65 (13)	5646 (7)
C(4N1)	8427 (22)	-744 (12)	2304 (6)	C(4N2)	7919 (24)	-232 (14)	4996 (7)

the structure consists of two crystallographically independent half clusters of Ru atoms and their carbonyl ligands plus two independent tetramethylammonium cations. The clusters are situated on the mirror plane at  $y = \frac{1}{4}$ . Inspection of Fig. 1 and comparison of bond lengths and angles shows that although the two clusters are similar, they have differing orientations with respect to the *a* and *c* axes. The stereochemistry of either anion is represented in Fig. 2. The mirror plane includes Ru(2)···Ru(5) and the carbonyl groups associated with C(5), C(7), and C(10). The octahedral Ru framework is very nearly regular. Average non-bridged and bridged Ru—Ru distances of 2.903 and 2.852 Å, respectively, show a slight shortening of the Ru—Ru bond with bridging. Similar shortenings (2.907 and 2.855 Å) have been observed in  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$  (Sirigu, Bianchi & Benedetti, 1969) and in the non-carbido hexaruthenium cluster  $[\text{Ru}_6(\text{CO})_{18}\text{H}_2]$  (2.954 and 2.867 Å) (Churchill & Wormald, 1971). The carbido C atom lies close to the geometric center of the cluster and is six

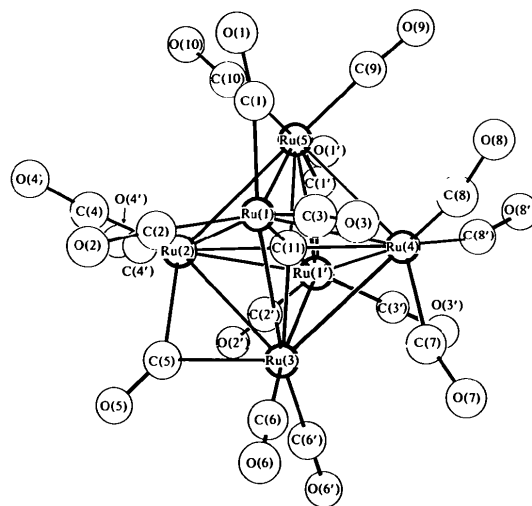


Fig. 2. A general view of the  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  anion showing the labelling system.

Table 2. Bond lengths (Å)

Average C—O in bridging groups = 1.19 (2) Å. Average C—O in terminal groups = 1.19 (4) Å. Average N—C in the two tetramethylammonium cations = 1.51 (3) Å.

	Cluster A	Cluster B
(1) Ru—Ru		
Ru(1)—Ru(2)	2.889 (1)	2.917 (1)
Ru(1)—Ru(3)	2.914 (1)	2.933 (1)
Ru(1)—Ru(4)	2.880 (1)	2.861 (1)
Ru(1)—Ru(5)	2.863 (1)	2.848 (1)
Ru(2)—Ru(3)	2.857 (1)	2.832 (1)
Ru(3)—Ru(4)	2.895 (1)	2.908 (1)
Ru(4)—Ru(5)	2.886 (1)	2.849 (1)
Ru(5)—Ru(2)	2.923 (1)	3.001 (1)
(2) Ru—C in semi-bridging CO groups		
Ru(1) C(1)	1.933 (15)	1.954 (16)
Ru(5)—C(1)	2.303 (15)	2.290 (16)
Ru(2)—C(5)	2.026 (18)	2.028 (18)
Ru(3)—C(5)	2.179 (18)	2.030 (18)
(3) Ru—C in terminal CO groups		
Ru(1)—C(2)	1.826 (14)	1.821 (16)
Ru(1)—C(3)	1.832 (15)	1.851 (15)
Ru(2)—C(4)	1.823 (17)	1.771 (20)
Ru(3)—C(6)	1.812 (17)	1.798 (18)
Ru(4)—C(7)	1.787 (43)	1.862 (29)
Ru(4)—C(8)	1.757 (27)	1.808 (18)
Ru(5)—C(9)	1.821 (19)	1.767 (19)
Ru(5)—C(10)	1.840 (18)	1.837 (19)
(4) Ru—C of the carbido-C atom		
Ru(1)—C(11)	2.038 (13)	2.038 (14)
Ru(2)—C(11)	2.038 (13)	2.036 (14)
Ru(3)—C(11)	2.064 (13)	2.042 (14)
Ru(4)—C(11)	2.044 (13)	2.058 (14)
Ru(5)—C(11)	2.029 (13)	2.061 (14)

coordinate. Ru—C distances are in the range 2.037–2.053 Å and Ru—C—Ru angles are nearly linear (177.0–178.8°). Again these are similar to values of 2.05 Å in  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$  (Sirigu, Bianchi & Benedetti, 1969) and 2.04 Å  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{arene})]$  (Mason & Robinson, 1968), and correspond to an Ru—C<sup>2+</sup> covalent bond (Mason & Robinson, 1968). Five of the Ru atoms have two terminal CO ligands (Ru—C—O =

175.7–179.0°); Ru(4) has two terminal carbonyls which are clearly bonded linearly [Ru(4)—C(8)—O(8) = 169.9° × 2] and one which has an Ru(4)—C(7)—O(7) angle of 159.9°. The large thermal factors of C(7) and O(7) and the short non-bonded Ru(3)···C(7) distances (2.615 Å) indicate that this terminal carbonyl is disordered. Ru—C distances are in the range 1.783–1.842 Å and are shorter than the 1.92 Å found in  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{arene})]$  (Mason & Robinson, 1968). The three non-terminal carbonyls are semi-bridging since they are placed asymmetrically between two Ru atoms [C(1)—Ru(1) 1.944, C(1)—Ru(5) 2.297 Å; C(5)—Ru(2) 2.027, C(5)—Ru(3) 2.105 Å]. Ru—C—O angles deviate considerably from linearity and range from 128.5 to 147.2°. The Ru—C distances are longer than those associated with terminal carbonyls, but C—O lengths of 1.177–1.197 Å are comparable with those of the terminal groups, 1.153–1.238 Å. One short non-bonded contact between O(4)(*x,y,z*)*A* and C(1N2)(1.5 - *x*, -*y*, -0.5 + *z*) of 2.903 Å is noted. The remaining intermolecular distances are consistent with normal van der Waals packing radii. Bond lengths and angles in both tetramethylammonium cations are normal, but disorder is indicated in one of them, as was found in  $[(\text{CH}_3)_4\text{N}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ . They are packed in layers close to the *y* = 0 and *y* = ½ planes. The structure may thus be described as alternating layers of tetramethylammonium ions centered at *y* ≈ 0, ½ and metal clusters centered at *y* = 0.25, 0.75 stacked along the *b* axis. Examination of Fig. 1 shows that stacking gives a 6:12 coordination pattern.

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