

## The Structure of a Dinuclear Complex of Osmium(I) with a Metal-to-Metal Single Bond: Bis-( $\mu$ -acetato)hexacarbonyldiosmium

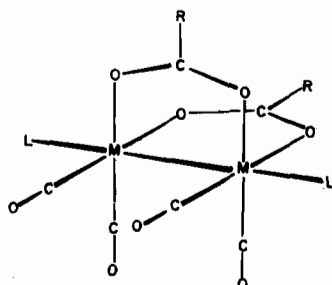
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The crystal and molecular structure of bis-( $\mu$ -acetato)hexacarbonyldiosmium,  $(\text{CH}_3\text{CO}_2)_2\text{Os}_2(\text{CO})_6$ , has been determined from the intensities of 3919 independent reflections measured with a counter diffractometer. The compound crystallizes in the monoclinic space group  $P2_1/c$  with eight molecules in a unit cell of dimensions  $a=7.767(6)$ ,  $b=28.347(14)$ ,  $c=14.600(6)$  Å and  $\beta=103.16(2)$ ;  $\rho_{\text{obs}}=2.83$  and  $\rho_{\text{calcd}}=2.816$  g/ml. The structure was solved by Patterson and Fourier methods and refined by least squares to a conventional  $R$  factor of 9.2% and a weighted  $R$  of 8.9%. The crystal structure is composed of dinuclear molecular units with no crystallographically imposed symmetry. The two independent molecules are identical within their estimated standard deviations and each has approximately  $C_{2v}$  symmetry with cisoid bridging acetate groups. The coordination about each osmium atom is roughly octahedral and the Os—Os distance is 2.731(2) Å.

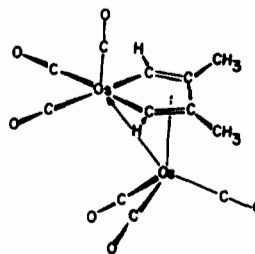
### Introduction

Crooks, *et al.*,<sup>1</sup> have recently published the synthesis of a series of polynuclear carboxylate complexes of ruthenium and osmium carbonyls. On the basis of mass spectral, NMR and IR evidence, they have postulated dinuclear molecules, I and II, of  $C_{2v}$  symmetry. The crystal structure of one of these compounds,  $(\text{CH}_3\text{CO}_2)_2\text{Ru}_2(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$ , has been determined by B. T. Kilbourn.<sup>2</sup> It has the postulated  $C_{2v}$  structure, II. The planes of the pyridine rings are found to be perpendicular to the mirror plane containing the Ru atoms. We report here the crystal



I, L=CO  
II, L=py

structure of bis-( $\mu$ -acetato)hexacarbonyldiosmium, the molecules of which have a structure of type I.



III

The only structures published to date that contain osmium-osmium single bonds are  $\text{Os}_3(\text{CO})_{12}$ <sup>3</sup> and  $\text{C}_6\text{H}_8\text{Os}_2(\text{CO})_6$ <sup>4</sup> (with the structure III), although it has been reported<sup>5</sup> that  $(h^5\text{-C}_5\text{H}_5)_2\text{Os}_2(\text{CO})_4$  is under study. On the basis of the inert gas formalism,  $(\text{CH}_3\text{CO}_2)_2\text{Os}_2(\text{CO})_6$ , which contains osmium(I) would be expected to have an osmium-osmium single bond. One objective of this investigation was to determine accurately the length of that bond, thereby making a contribution to the store of information on the lengths of metal-metal bonds of various orders. Another reason for our interest in this structure was to use it in a broader study of the interpretation of intra- and intermolecular vibrational coupling constants in metal carbonyl molecules.

### Experimental Section

Well formed, clear, white crystals of  $(\text{CH}_3\text{CO}_2)_2\text{Os}_2(\text{CO})_6$  were kindly supplied by Professor J. Lewis and Dr. B.F.G. Johnson. Precession films of the  $h0\ell$  and  $h1\ell$  levels and Weissenberg films of the  $0k\ell$  and  $1k\ell$  levels showed the crystal to be monoclinic with systematic absences along  $0k0$  for  $k=2n+1$  and in the  $h0\ell$  zone for  $\ell=2n+1$  conforming to the space group  $P2_1/c$  ( $C_{2h}^{52}$ , No. 14). Unit cell dimensions were determined using Mo  $K\alpha$  radiation ( $\lambda=0.7107$  Å) on a General Electric XRD-6 automated diffractometer by least squares refinement<sup>6</sup> of the accurately measured angular settings of 36 reflec-

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(2) B.T. Kilbourn, unpublished results, privately communicated.

tions. The dimensions are:  $a=7.767(6)$ ,  $b=28.347(14)$ ,  $c=14.600(6)$  Å, and  $\beta=103.16(2)^\circ$ .<sup>7</sup> The density was measured by flotation in a thallose formate to be  $\rho_o=2.83(3)$  g/ml. The calculated density,  $\rho_c$ , is 2.816 g/ml for  $Z=8$ . With  $Z=8$  there are two independent dinuclear molecules in the asymmetric unit and no crystallographic symmetry is imposed on either.

A capped prismatic crystal of approximate dimensions 0.125 mm by 0.16 mm by 0.12 mm was mounted on a General Electric XRD-6 automated diffractometer with the 4 12 1 vector coincident with the  $\Phi$  axis. Intensities were measured with a scintillation counter using Ni-filtered Cu  $K\alpha$  radiation with a take off angle of  $2^\circ$ . The pulse height discriminator was set to receive 95% of the Cu  $K\alpha$  peak. Scans were of the  $\theta-2\theta$  type with a scan rate of  $2^\circ/\text{min}$ . The angular width of the scans varied as a function of the separation between the  $\alpha_1$  and  $\alpha_2$  reflections and included the region from  $0.6^\circ$  below the  $K\alpha_1$  peak to  $0.6^\circ$  above the  $K\alpha_2$  peak for each reflection. Backgrounds were estimated by counting for 20 seconds at each end of the scan. The intensities of 4508 independent reflections within the sphere bounded by  $2\theta=110^\circ$  were collected. Of these, 59 of the last 500 reflections collected were rejected because of an instrumental malfunction. There were 547 reflections which had an intensity,  $I = P - B_1 - B_2$  where  $P$  is the peak count and  $B_1$  and  $B_2$  are the scaled background counts, less than  $1/2\sigma_I$ ,  $\sigma_I = (P + B_1 + B_2)^{1/2}$ . Their intensities were set equal to  $1/2\sigma_I$ . Four reflections were remeasured at intervals of 75 reflections throughout the data collection as a check on instrumental and crystal stability. A slight decrease in intensity with time was linear and did not differ statistically for the four reflections within the limits of counting statistics,  $\sigma_I$ , and a five percent machine error, derived from the scatter of the standard reflections about the least squares line through them. The crystal alignment was checked midway through the data collection process and it had not shifted significantly. The most probable cause of this decrease is slow crystal decomposition, a supposition supported by the observation of clouding in the crystal after the completion of data collection.

The corrected intensities were used to calculate structure factor amplitudes,  $|F_o|$ , and their standard deviations,  $\sigma_F$ . The quantities are defined by the expressions

$$|F_o| = (I/Lp)^{1/2}$$

$$\sigma_F = [\sigma_I^2 + (0.05I)^2]^{1/2} / (2Lp|F_o|)$$

in which  $Lp$  represents the Lorentz-polarization correction. Because of the large linear absorption coefficient,  $\mu=309.6 \text{ cm}^{-1}$ , the ten crystal faces were measured both on the diffractometer and under a stereo-

scopic microscope with a calibrated eye piece (max. resolution 0.01 mm) and an absorption correction applied. Transmission factors varied from 0.057 to 0.157.

Atomic scattering factors for osmium(I) were those of Thomas and Umeda<sup>8</sup> and for carbon and oxygen were those of Cromer and Waber.<sup>9</sup> All were corrected for the real and imaginary part of the anomalous dispersion using the values of Cromer and Liberman.<sup>10</sup>

The positions of the four independent osmium atoms were located from a three-dimensional map of the Patterson function. Least squares refinement of the osmium atoms gave  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.331$  and  $R_2 = [\sum w_F |F_o| - |F_c|]^2 / \sum w_F |F_o|^2]^{1/2} = 0.305$  where the weights  $w_F = \sigma_F^{-2}$ . Anisotropic thermal parameters were refined for the osmium atoms, a difference Fourier was computed and the positions of the remaining 40 non-hydrogen atoms were determined. Diagonal refinement of these 44 atoms gave  $R_1 = 0.116$  and  $R_2 = 0.119$ . Zachariasen's betas<sup>11</sup> were calculated for the 362 most intense reflections and the last 530 reflections measured were rejected because of an intermittent machine error. Full matrix least squares refinement was then continued using the 3919 remaining reflections and assigning anisotropic thermal parameters to the osmium atoms only, until all parameter shifts were less than half their e.s.d.'s except for the secondary extinction parameter which was just slightly less than its e.s.d. The magnitude of the structure factor of the most intense reflection was reduced by a factor of 0.47 by secondary extinction.

The final R values were:  $R_1 = 0.092$  and  $R_2 = 0.089$ . The factors limiting this refinement are probably the accuracy of the absorption correction or the possibility of anisotropic secondary extinction. It also seems likely that if refinement were to be continued with anisotropic thermal parameters for all non-hydrogen atoms much lower R values could be reached, without any real change in the structure or improvement in accuracy. The e.s.d. of an observation of unit weight is 2.218 and the quantity  $w_F |F_o| - |F_c|$  did not vary systematically with either  $|F_o|$  or  $\sin \theta/\lambda$ . A difference Fourier synthesis was computed using the final parameters. The largest peak, in the vicinity of one of the osmium atoms, was 1.39 electrons/Å<sup>3</sup>. The standard deviation in electron density was 0.3 e/Å<sup>3</sup>. Distances and angles were calculated and their e.s.d.'s include all correlations between unit cell constants and all correlations between atomic positions greater than 0.1.

## Results

Table I is a list of the final values of  $|F_c|$  and  $|F_o|$  scaled to  $F_c$ . Fractional atomic coordinates and thermal parameters are given in Table II. Significant intramolecular distances and angles and their averages are given in Tables III-V. Figures 1 and 2 show two perspective views of the molecule and Figure 3 illu-

(6) Computer programs used in the structure determination include: PICK2 (I. A. Ibers), for refining cell constants and generating diffractometer settings; DIFDAR (A.S. Parks), for data reduction; ABCOR (N.W. Alcock, B. Lee, and V. Day), for the absorption correction (with secondary extinction corrections added locally); FORDAP (A. Zalkin) for Patterson and Fourier syntheses; SFIX (a local revision of C.T. Prewitt's SFLS-5) for full-matrix least squares refinement minimizing  $w_F |F_o| - |F_c|$ ; SDIAG (a locally modified version of SFLS-5) for diagonal least squares refinement; ORTEP (C.K. Johnson), for figures; STANI (B.G. DeBoer) for computing distances and angles.

(7) The values in parentheses are the estimated standard deviations in units of the last significant figure.

(8) I.H. Thomas and K. Umeda, *J. Chem. Phys.*, 26, 239 (1957).  
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 (11) W.R. Zachariasen, *Acta Cryst.*, 16, 1139 (1963).

Table I. Calculated and Observed Structure Factors (x 5).

h	k	l	F <sub>obs</sub>	F <sub>calc</sub>	h	k	l	F <sub>obs</sub>	F <sub>calc</sub>	h	k	l	F <sub>obs</sub>	F <sub>calc</sub>	h	k	l	F <sub>obs</sub>	F <sub>calc</sub>
0	0	0	100	100	0	0	0	100	100	0	0	0	100	100	0	0	0	100	100
0	0	1	100	100	0	0	1	100	100	0	0	1	100	100	0	0	1	100	100
0	0	2	100	100	0	0	2	100	100	0	0	2	100	100	0	0	2	100	100
0	0	3	100	100	0	0	3	100	100	0	0	3	100	100	0	0	3	100	100
0	0	4	100	100	0	0	4	100	100	0	0	4	100	100	0	0	4	100	100
0	0	5	100	100	0	0	5	100	100	0	0	5	100	100	0	0	5	100	100
0	0	6	100	100	0	0	6	100	100	0	0	6	100	100	0	0	6	100	100
0	0	7	100	100	0	0	7	100	100	0	0	7	100	100	0	0	7	100	100
0	0	8	100	100	0	0	8	100	100	0	0	8	100	100	0	0	8	100	100
0	0	9	100	100	0	0	9	100	100	0	0	9	100	100	0	0	9	100	100
0	0	10	100	100	0	0	10	100	100	0	0	10	100	100	0	0	10	100	100
0	0	11	100	100	0	0	11	100	100	0	0	11	100	100	0	0	11	100	100
0	0	12	100	100	0	0	12	100	100	0	0	12	100	100	0	0	12	100	100
0	0	13	100	100	0	0	13	100	100	0	0	13	100	100	0	0	13	100	100
0	0	14	100	100	0	0	14	100	100	0	0	14	100	100	0	0	14	100	100
0	0	15	100	100	0	0	15	100	100	0	0	15	100	100	0	0	15	100	100
0	0	16	100	100	0	0	16	100	100	0	0	16	100	100	0	0	16	100	100
0	0	17	100	100	0	0	17	100	100	0	0	17	100	100	0	0	17	100	100
0	0	18	100	100	0	0	18	100	100	0	0	18	100	100	0	0	18	100	100
0	0	19	100	100	0	0	19	100	100	0	0	19	100	100	0	0	19	100	100
0	0	20	100	100	0	0	20	100	100	0	0	20	100	100	0	0	20	100	100
0	0	21	100	100	0	0	21	100	100	0	0	21	100	100	0	0	21	100	100
0	0	22	100	100	0	0	22	100	100	0	0	22	100	100	0	0	22	100	100
0	0	23	100	100	0	0	23	100	100	0	0	23	100	100	0	0	23	100	100
0	0	24	100	100	0	0	24	100	100	0	0	24	100	100	0	0	24	100	100
0	0	25	100	100	0	0	25	100	100	0	0	25	100	100	0	0	25	100	100
0	0	26	100	100	0	0	26	100	100	0	0	26	100	100	0	0	26	100	100
0	0	27	100	100	0	0	27	100	100	0	0	27	100	100	0	0	27	100	100
0	0	28	100	100	0	0	28	100	100	0	0	28	100	100	0	0	28	100	100
0	0	29	100	100	0	0	29	100	100	0	0	29	100	100	0	0	29	100	100
0	0	30	100	100	0	0	30	100	100	0	0	30	100	100	0	0	30	100	100

Table I. (Continued)

Table with multiple columns containing numerical data and chemical symbols (e.g., F, O, S, C, H, N, P, K, L, M, R, T, U, V, W, X, Y, Z). The table is organized in a grid-like structure with rows and columns.

**Table II.** A. Fractional Coordinates and Isotropic Temperature Factors <sup>a</sup>

Atom	x	y	z	B(A <sup>2</sup> ) <sup>b</sup>
OsA1	0.6939(1)	-0.24141(3)	0.16418(7)	4.6
OsA2	0.4662(1)	-0.23329(4)	0.28082(8)	5.7
CA01	0.851 (4)	-0.2587 (10)	0.081 (2)	8.6(7)
OA01	0.947 (3)	-0.2681 (8)	0.038 (2)	11.3(7)
CA02	0.294 (5)	-0.2393 (11)	0.364 (3)	9.8(9)
OA02	0.212 (4)	-0.2466 (11)	0.411 (2)	15.5(9)
CA03	0.584 (3)	-0.1991 (8)	0.084 (2)	5.5(5)
OA03	0.516 (3)	-0.1702 (8)	0.033 (2)	10.9(6)
CA04	0.582 (3)	-0.1844 (8)	0.347 (2)	5.4(5)
OA04	0.655 (3)	-0.1520 (7)	0.385 (1)	9.0(5)
CA05	0.837 (3)	-0.1972 (8)	0.227 (2)	5.4(5)
OA05	0.935 (3)	-0.1706 (8)	0.269 (1)	9.6(5)
CA06	0.336 (3)	-0.1924 (8)	0.208 (2)	5.9(5)
OA06	0.243 (3)	-0.1667 (8)	0.157 (2)	10.8(6)
CA07	0.523 (2)	-0.2943 (5)	0.188 (1)	5.7(3)
OA10	0.353 (2)	-0.12916(6)	0.207 (1)	7.0(4)
CA07	0.394 (4)	-0.3095 (9)	0.138 (2)	6.7(6)
CA09	0.292 (4)	-0.3537 (12)	0.093 (2)	10.5(9)
OA09	0.809 (2)	-0.2941 (5)	0.256 (1)	5.8(3)
CA08	0.633 (2)	-0.2839 (6)	0.360 (1)	6.3(4)
OA08	0.755 (3)	-0.3055 (9)	0.330 (2)	7.0(5)
CA10	0.838 (4)	-0.3456 (11)	0.395 (2)	10.2(8)
OsB1	0.0956(1)	-0.01283(4)	0.19319(7)	4.9
OsB2	-0.1381(1)	-0.01324(3)	0.30759(7)	4.6
CB01	0.261 (4)	-0.0021 (9)	0.115 (2)	7.1(6)
OB01	0.354 (3)	0.0053 (7)	0.070 (1)	10.6(6)
CB02	-0.306 (4)	-0.0016 (10)	0.385 (2)	7.4(6)
OB02	-0.388 (3)	0.0080 (8)	0.436 (2)	12.2(7)
CB03	-0.010 (3)	-0.0608 (9)	0.119 (2)	6.5(6)
OB03	-0.079 (3)	-0.0936 (8)	0.076 (2)	10.5(6)
CB04	-0.027 (3)	-0.0588 (7)	0.383 (1)	4.3(4)
OB04	0.039 (3)	-0.0893 (7)	0.428 (1)	8.2(5)
CB05	0.233 (3)	-0.0539 (8)	0.268 (2)	5.6(5)
OB05	0.325 (3)	-0.0814 (8)	0.318 (2)	10.7(6)
CB06	-0.281 (3)	-0.0579 (8)	0.236 (2)	6.0(5)
OB06	-0.377 (2)	-0.0847 (7)	0.189 (1)	9.3(5)
OB09	-0.072 (2)	0.0382 (6)	0.116 (1)	6.9(4)
OB08	-0.246 (2)	0.0423 (6)	0.222 (1)	6.8(4)
CB08	-0.205 (3)	0.0564 (8)	0.148 (2)	6.2(5)
CB10	-0.320 (4)	0.0960 (11)	0.089 (2)	9.5(8)
OB10	0.024 (2)	0.0394 (5)	0.379 (4)	5.4(3)
OB07	0.199 (2)	0.0444 (5)	0.275 (1)	5.7(3)
CB07	0.156 (3)	0.0590 (8)	0.351 (2)	6.5(5)
CB09	0.249 (3)	0.1023 (9)	0.400 (2)	8.0(6)

B. Anisotropic Temperature Factors <sup>c</sup>

Atom	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
OsA1	5.231(54)	4.566(52)	4.133(48)	0.932(39)	1.340(38)	0.164(36)
OsA2	5.057(54)	5.576(58)	4.849(53)	0.426(41)	1.686(41)	-0.612(40)
OsB1	5.093(54)	5.390(57)	4.430(51)	-0.125(40)	1.302(40)	-0.555(38)
OsB2	4.967(53)	4.194(50)	4.957(52)	0.055(37)	1.532(40)	0.171(37)

<sup>a</sup> Numbers in parentheses are e.s.d.'s in the last figure. <sup>b</sup> Effective isotropic B's are given for the anisotropically refined atoms. <sup>c</sup> The form of the temperature-factor expression is:  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

strates the packing of the molecules in the unit cell. The two crystallographically independent molecules and all atoms therein are distinguished by the labels A and B.

**Discussion**

The molecular structure of  $(CH_3CO_2)_2Os_2(CO)_6$  is that which Crooks, *et al.*<sup>1</sup> anticipated. Each of the two independent molecules has approximate  $C_{2v}$  symmetry but this is not crystallographically imposed. The various bond lengths and angles may be sorted into sets, each set containing those which would be iden-

tical if the two molecules were, rigorously, (a) identical, and (b) of perfect  $C_{2v}$  symmetry. It is then found that there is very little variance within each set. Specifically, the values in each set are within 3 e.s.d.'s or less of the average value for the set, with the exception of three types of angle: Os—Os—CO(eq), Os—Os—O(acetate) and Os—O—C(acetate). Although these deviations are statistically significant, there appears to be no pattern of distortion and the average values of these as well as all other dimensions will be used for discussion of the structure.

The overall  $C_{2v}$  molecular structure incorporates six-fold coordination about the osmium atoms with cisoid bridging acetate groups. The axial carbonyl groups are not colinear with the Os—Os bond but are

**Table III.** Individual Bond Distances A <sup>a</sup>.

OsA1-OsA2	2.730(02)	CA02-OA02	1.055(46)
OsB1-OsB2	2.732(02)	CB01-OB01	1.106(31)
OsA1-CA01	1.970(32)	CB02-OB02	1.115(33)
OsA2-CA02	2.006(40)	CA03-OA03	1.148(26)
OsB1-CB01	1.926(28)	CA04-OA04	1.159(24)
OsB2-CB02	1.939(29)	CA05-OA05	1.146(26)
OsA1-CA03	1.759(23)	CA06-OA06	1.167(25)
OsA1-CA05	1.781(22)	CB03-OB03	1.179(27)
OsA2-CA04	1.804(23)	CB04-OB04	1.143(23)
OsA2-CA06	1.738(23)	CB05-OB05	1.186(26)
OsB1-CB03	1.818(26)	CB06-OB06	1.170(25)
OsB1-CB05	1.776(23)	OA07-CA07	1.330(29)
OsB2-CB04	1.782(20)	OA10-CA07	1.229(30)
OsB2-CB06	1.844(23)	OA08-CA08	1.284(27)
OsA1-OA07	2.080(14)	OA09-CA08	1.286(28)
OsA1-OA09	2.069(15)	OB07-CB07	1.291(28)
OsA2-OA08	2.097(15)	OB10-SB07	1.313(28)
OsA2-OA10	2.060(16)	OB08-CB08	1.256(26)
OsB1-OB07	2.066(15)	OB09-CB08	1.336(28)
OsB1-OB09	2.094(16)	CA07-CA09	1.550(38)
OsB2-OB08	2.066(16)	CA08-CA10	1.527(37)
OsB2-OB10	2.076(14)	CB07-CB09	1.518(33)
CA01-OA01	1.109(34)	CB08-CB10	1.562(37)

<sup>a</sup> Numbers in parentheses are e.s.d.'s occurring in the last significant digit.

**Table IV.** Selected Bond Angles.

OsA2-OsA1-CA01	170.6(9)	OB09-CB08-CB10	118(2)
OsA1-OsA2-CA02	170.2(10)	OB08-CB08-CB10	119(2)
OsB2-OsB1-CB01	171.2(8)	CA05-OsA1-OA09	92.8(8)
OsB1-OsB2-CB02	169.9(9)	CA03-OsA1-OA07	91.5(8)
OsA2-OsA1-CA03	94.4(8)	CA06-OsA2-OA10	95.3(9)
OsA2-OsA1-CA05	92.3(7)	CA04-OsA2-OA08	93.5(8)
OsA1-OsA2-CA04	94.8(7)	CB03-OsB1-OB09	93.1(9)
OsA1-OsA2-CA06	92.3(8)	CB05-OsB1-OB07	93.4(8)
OsB2-OsB1-CB03	95.2(8)	CB04-OsB2-OB10	93.4(7)
OsB2-OsB1-CB05	90.6(8)	CB06-OsB2-OB08	94.0(8)
OsB1-OsB2-CB04	94.7(7)	OA07-OsA1-OA09	84.9(6)
OsB1-OsB2-CB06	93.1(7)	OA08-OsA2-OA10	83.0(6)
OsA1-CA01-OA01	177(2)	OB07-OsB1-OB09	83.2(6)
OsA2-CA02-OA02	173(7)	OB08-OsB2-OB10	82.8(6)
OsB1-CB01-OB01	178(2)	OsA1-OA07-CA07	120(1)
OsB2-CB02-OB02	172(4)	OsA1-OA09-CA08	123(1)
OsA1-CA03-OA03	177(2)	OsA2-OA08-CA08	123(2)
OsA1-CA05-OA05	177(2)	OsA2-OA10-CA07	127(2)
OsA2-CA04-OB04	177(2)	OsB1-OB07-CB07	127(1)
OsA2-CA06-OB06	177(2)	OsB1-OB09-CB08	121(1)
OsB1-CB03-OB03	176(2)	OsB2-OB08-CB08	128(2)
OsB1-CB05-OB05	180(1)	OsB2-OB10-CB07	125(1)
OsB2-CB04-OB04	177(2)	CA01-OsA1-CA03	92(1)
OsB2-CB06-OB06	177(2)	CA01-OsA1-CA05	95(1)
OsA2-OsA1-OA07	84.6(6)	CA02-OsA2-CA04	94(1)
OsA2-OsA1-OA09	84.4(4)	CA02-OsA2-CA06	93(1)
OsA1-OsA2-OA08	83.0(5)	CB01-OsB1-CB03	92(1)
OsA1-OsA2-OA10	82.3(5)	CB01-OsB1-CB05	95(1)
OsB2-OsB1-OB07	82.7(4)	CB02-OsB2-CB04	93(1)
OsB2-OsB1-OB09	85.0(5)	CB02-OsB2-CB06	93(1)
OsB1-OsB2-OB08	82.2(5)	CA01-OsA1-OA07	88(1)
OsB1-OsB2-OB10	83.9(4)	CA01-OsA1-OA09	89(1)
OA07-CA07-OA10	125(2)	CA02-OsA2-OA08	91(1)
OA07-CA07-CA09	116(2)	CA02-OsA2-OA10	89(1)
OA10-CA07-CA09	118(2)	CB01-OsB1-OB07	90(1)
OA09-CA08-OA08	125(2)	CB01-OsB1-OB09	89(1)
OA09-CA08-CA10	112(2)	CB02-OsB2-OB08	89(1)
OA08-CA08-CA10	113(2)	CB02-OsB2-OB10	90(1)
OB07-CB07-OB10	121(2)	CA03-OsA1-CA05	91(1)
OB07-CB07-CB09	118(2)	CA04-OsA2-CA06	88(1)
OB10-CB07-CB09	121(2)	CB03-OsB1-CB05	90(1)
OB09-CB08-OB08	123(2)	CB04-OsB2-CB06	90(1)

tilted along the mirror plane toward the acetate groups.

**Table V.** Average Interatomic Distances and Angles <sup>a</sup>.

Os-Os	2.731(2)	O-Os-O(acetate)	83.5(4)
Os-C(ax)	1.96(2)	C(eq)-Os-O(acetate)	93.0(5)
Os-C(eq)	1.79(1)	C(eq)-Os-C(eq)	89.7(7)
Os-O	2.076(6)	C(ax)-Os-C(eq)	93.5
C-O(ax)	1.10(2)	C(ax)-Os-O(acetate)	89.5(4)
C-O(eq)	1.16(1)	Os-C-O(ax)	175(3)
O-C(acetate)	1.29(1)	Os-C-O(eq)	177(1)
C-CH <sub>3</sub>	1.54(2)	O-C-O(acetate)	124(1)
Os-Os-C(ax)	170.5(6)	O-C-CH <sub>3</sub> (acetate)	118(1)
Os-Os-C(eq)	93.4(3)	Os-O-C(acetate)	124(1)
Os-Os-O(acetate)	83.5(2)		

<sup>a</sup> Numbers in parentheses are rms e.s.d.'s occurring in the last significant digit.

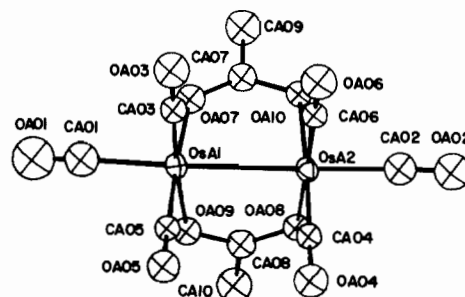
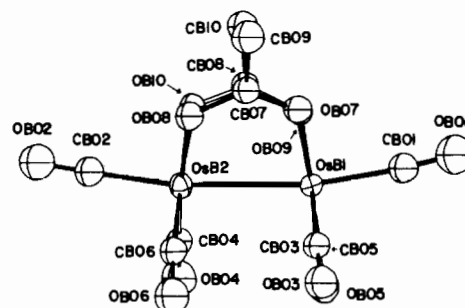
Figure 1. A view of molecule A down the C<sub>2</sub> axis.

Figure 2. A view of molecule B perpendicular to the mirror plane containing the osmium atoms.

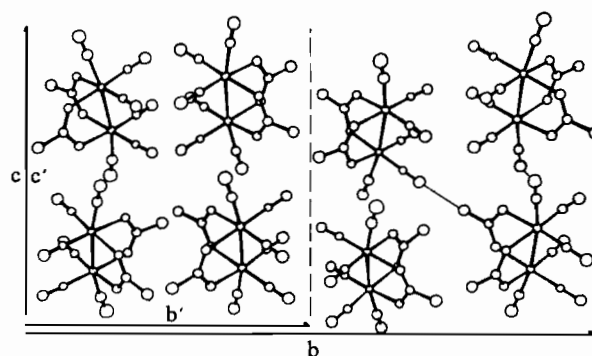


Figure 3. A projection of the contents of the unit cell on the bc plane. b and c are the lengths of the b and c axes. b' and c' are the lengths of the b and c axes in the higher space group C2/c.

The Os—Os distance of 2.731 Å is consistent with a description of the bonding in this molecule which assigns 18 electrons to the valence orbitals (5d, 6s, 6p) of each osmium atom and requires an Os—Os

**Table VI.** Significant Dimensions in two  $[M(\text{RCO}_2)(\text{CO})_2\text{L}]_2$  Compounds.

Ru-Ru	2.678 Å	Os-Os	2.731 Å
Ru-C(eq)	1.84 Å	Os-C(eq)	1.96 Å
C-O(eq)	1.15 Å	C-O(eq)	1.16 Å
Normal to		Normal to	
Ru(CO) <sub>2</sub> and Ru-Ru	6.9°	Os(CO) <sub>2</sub> and Os-Os	4.8°
OC-Ru-CO	88.56°	OC-Os-CO	89.7°
O-Ru-O	83.57°	O-Os-O	83.5°

single bond. This distance is close to that reported<sup>4</sup> for  $\text{C}_6\text{H}_8\text{Os}_2(\text{CO})_6$  (2.74 Å) and significantly shorter than the value of 2.88 Å reported<sup>3</sup> for  $\text{Os}_3(\text{CO})_{12}$ .

The bridging acetate groups are planar and the O---O distance within the acetate group is 2.28 Å, almost 0.5 Å shorter than the Os—Os bond. This necessarily causes distortions from 90° angles in the six-fold coordination about the osmium. The average angle between the Os—Os bond and the normals to the planes defined by O7—Os1—O9 and O8—Os2—O10 is 8.7(5)°. Similarly, the angles between the normals to the planes defined by each osmium atom and its equatorial carbonyl groups and the Os—Os bond have an average value of 4.8(5)°. The axial carbonyl groups are bent towards the acetate groups, with a mean Os—Os—C angle of 170.5°.

As expected from their chemical reactivity, the axial carbonyl groups are more weakly bound to the metal than are the equatorial ones. The average Os—C distance to equatorial carbonyl groups is 1.79 Å, while that to the axial carbonyl groups is 1.96 Å. The Os—C distance to the equatorial carbonyls is shorter than those found in the Os<sup>2+</sup> compounds  $\text{Os}_3(\text{CO})_{12}$  (1.95 Å)<sup>3</sup> and  $\text{Os}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$  (1.90 and 1.93 Å).<sup>12</sup>

(12) J.K. Stalick and J.A. Ibers, *Inorg. Chem.*, 8, 419 (1969).

This structure is very similar to that of  $(\text{CH}_3\text{CO}_2)_2\text{Ru}_2(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$ .<sup>2</sup> A comparison of certain dimensions is given in Table VI. There appear to be no significant differences that are not ascribable to the difference in metal and in the axial substituent. However, consequences of these two changes cannot be identified independently at this time.

The packing of the molecules in the unit cell, Figure 3, exhibits pseudosymmetry. It is as if the *b* axis were 14 Å long instead of 28 Å. If this were true, with the two-fold screw axis reducing to a simple two-fold axis, the molecule would have crystallographic C<sub>2</sub> symmetry. Similarly, on a glide at  $y = -1/8$  or, equivalently, an inversion center at  $x = 1/4$ ,  $y = -1/8$  and  $z = 1/4$  would relate the coordinates of molecule A to those of molecule B in Table II. The space group which would be formed if this pseudosymmetry were rigorous is I2/a, a nonstandard setting of C2/c, with a half molecule instead of two molecules as the asymmetric unit. The deviations from this more ordered array cause the closest intermolecular contacts. For example, the distances between the oxygen atoms of the axial carbonyls are 2.87 Å for OB02-OB02, 3.38 Å for OB01-OB01 and 3.10 Å for OA01-OA02. The deviations from the C<sub>2v</sub> averaged values for the three angles Os—Os—CO(eq), Os—Os—O(acetate) and Os—O—C(acetate) are not entirely due to the deviations from the more ordered structure. They result also, in part, from a C<sub>2v</sub> to C<sub>2</sub> distortion, which reduces the contacts between the equatorial carbonyls and the methyl groups as in the CA03-CB10 close contact.

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