selected bond distances and angles in Table III.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant AFOSR-85-0228. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990).

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **6a** (4 pages); a listing of observed and calculated structure factors for **6a** (20 pages). Ordering information is given on any current masthead page.

Structure and Bonding in Transition-Metal Carbonyls and Nitrosyls. 3. Molecular Structure of Osmium Pentacarbonyl from Gas-Phase Electron Diffraction

Jinfan Huang,[1a] Kenneth Hedberg,*[,1a] and Roland K. Pomeroy[1b]

Departments of Chemistry, Oregon State University, Corvallis, Oregon 97331, and Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received April 15, 1988

The molecular structure of osmium pentacarbonyl has been investigated by gas-phase electron diffraction. Corrections for three-atom multiple scattering were included. The data are consistent with a molecule of D_{3h} symmetry. Although the relative lengths of the axial and equatorial Os–C bonds could not be determined because of high correlations with several other parameters, the weight of the evidence strongly suggests that the axial bonds are the longer. Values for the bond lengths (r_g and r_α; r_α should be comparable to distances determined by X-ray diffraction) and some of the principal vibrational amplitudes (l) with estimated 2σ uncertainties are $\langle r_g(\mathrm{Os{-}C})\rangle = 1.962\ (4)$ Å, $\langle r_\alpha(\mathrm{Os{-}C})\rangle = 1.955\ (4)$ Å, $\Delta r_g(\mathrm{Os{-}C}) = r_g(\mathrm{Os{-}C_{ax}}) - r_g(\mathrm{Os{-}C_{eq}}) = 0.047\ (46)$ Å, $\Delta r_\alpha(\mathrm{Os{-}C}) = 0.043$ Å, $\langle r_g(\mathrm{C{\equiv}O})\rangle = 1.142\ (4)$ Å, $\langle r_\alpha(\mathrm{C{\equiv}O})\rangle = 1.130\ (4)$ Å, $\Delta r_g(\mathrm{C{\equiv}O}) = \langle r_\alpha(\mathrm{C{\equiv}O})\rangle = 0$ (assumed), $l(\mathrm{Os{-}C_{ax}}) = l(\mathrm{Os{-}C_{eq}}) - 0.003$ Å (assumed) $= 0.046\ (9)$ Å, $l(\mathrm{C{\equiv}O_{ax}}) = l(\mathrm{C{\equiv}O_{eq}})$ (assumed) $= 0.043\ (4)$ Å. The multiple scattering from $Os(CO)_5$ was found to be small, and although the quality of the fit was improved by inclusion of multiple scattering corrections, the parameter values obtained with and without them were not significantly different.

Introduction

Two types of structure dominate the shapes of inorganic five-coordinate molecules in the gas phase, the tetragonal pyramid and the trigonal bipyramid with respective symmetries C_{4v} and D_{3h}. As expected from the well-known valence-shell electron-pair repulsion (VSEPR) theory,[2] the halogen pentafluorides, such as BrF_5 and IF_5,[3] are of the first type and the pentahalides of atoms from group 15 and 5, such as PF_5,[4a] PCl_5,[4b] AsF_5,[4c] $SbCl_5$,[4d] VF_5,[4e] NbF_5,[4f] $NbCl_5$,[4g] TaF_5,[4f] $TaCl_5$,[4g] and $TaBr_5$[4h], are of the second. On the other hand, the pentahalides of atoms from group 6 appear to have distorted trigonal-bipyramidal structures (CrF_5[5a]) or to be a mixture of trigonal-bipyramidal and tetragonal-pyramidal forms ($MoCl_5$[5b] and WCl_5[5c]).

There are some interesting questions about the structures of the group 8 five-coordinate molecules. A number of investigations have confirmed that $Fe(CO)_5$ has D_{3h} symmetry both in the gas phase[6-9] and in the crystal.[10] There is controversy, however, about the relative lengths of the axial and equatorial Fe–C bonds: it has been concluded from the results of electron-diffraction studies[9] that, in contrast to what is found for other D_{3h} pentacoordinate molecules, the axial bonds in $Fe(CO)_5$ are the shorter. Work in this laboratory[11] revealed that the effects of vibrational averaging, which were not thoroughly investigated in the earlier diffraction work, play an especially important role in the determination of the relative bond lengths, and accordingly the relative bond lengths are still

---

(1) (a) Oregon State University. (b) Simon Fraser University.

(2) (a) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339. (b) Gillespie, R. J. *Molecular Geometry*; Van Nostrand-Reinhold: London, 1972.

(3) Heenan, R. K.; Robiette, A. G. *J. Mol. Struct.* **1979**, *55*, 191.

(4) (a) See, for example: Kurimura, H.; Yamamoto, S.; Egawa, T.; Kuchitsu, K. *J. Mol. Struct.* **1986**, *140*, 79 and references cited therein. (b) Adams, W. J.; Bartell, L. S. *J. Mol. Struct.* **1971**, *8*, 23. See also: McClelland, B. W.; Hedberg, L.; Hedberg, K. *J. Mol. Struct.* **1983**, *99*, 309. (c) Clippard, F. B.; Bartell, L. S. *Inorg. Chem.* **1970**, *9*, 805. (d) Ivashkevich, L. S.; Ischenko, A. A.; Spiridonov, V. P.; Strand, T. G.; Ivanov, A. A.; Nikolaev, A. N. *Zh. Strukt. Khim.* (*Engl. Transl.*) **1982**, *23*, 295. (e) Hagen, K.; Gilbert, M. M.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1982**, *21*, 2690. (f) Petrova, V. N.; Girichev, G. V.; Petrov, V. M.; Goncharuk, V. K. *Zh. Strukt. Khim.* (*Engl. Transl.*) **1985**, 26, 192. (g) Ischenko, A. A.; Strand, T. G.; Demidov, A. V.; Spiridonov, V. P. *J. Mol. Struct.* **1978**, *43*, 227. (h) Demidov, A. V.; Ivanov, A. A.; Ivashkevich, L. S.; Ischenko, A. A.; Spiridonov, V. P.; Almlöf, J.; Strand, T. G. *Chem. Phys. Lett.* **1979**, *64*, 528.

(5) (a) Jacob, E. J.; Hedberg, L.; Hedberg, K.; Davis, H.; Gard, G. L. *J. Phys. Chem.* **1984**, *88*, 1935. (b) Brunvoll, J.; Ischenko, A. A.; Spiridonov, V. P.; Strand, T. G. *Acta Chem. Scand., Ser. A*, in press. (c) Ezhov, Yu. S.; Sarvin, A. P. *Zh. Strukt. Khim.* (*Engl. Transl.*) **1983**, *24*, 140.

(6) Davis, M.; Hanson, H. P. *J. Phys. Chem.* **1965**, *69*, 3405.

(7) Beagley, B.; Cruickshank, D. W. J.; Pinder, P. M.; Robiette, A. G.; Sheldrick, G. M. *Acta Crystallogr., Sect. B*: *Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 737.

(8) Almenningen, A.; Haaland, A.; Wahl, K. *Acta Chem. Scand.* **1969**, *23*, 2245.

(9) Beagley, B.; Schmidling, D. G. *J. Mol. Struct.* **1974**, *22*, 466.

(10) (a) Hanson, A. W. *Acta Crystallogr.* **1962**, *15*, 930. (b) Donohue, J.; Caron, A. *Acta Crystallogr.* **1964**, *17*, 663.

(11) Unpublished work.

0276-7333/88/2307-2049$01.50/0

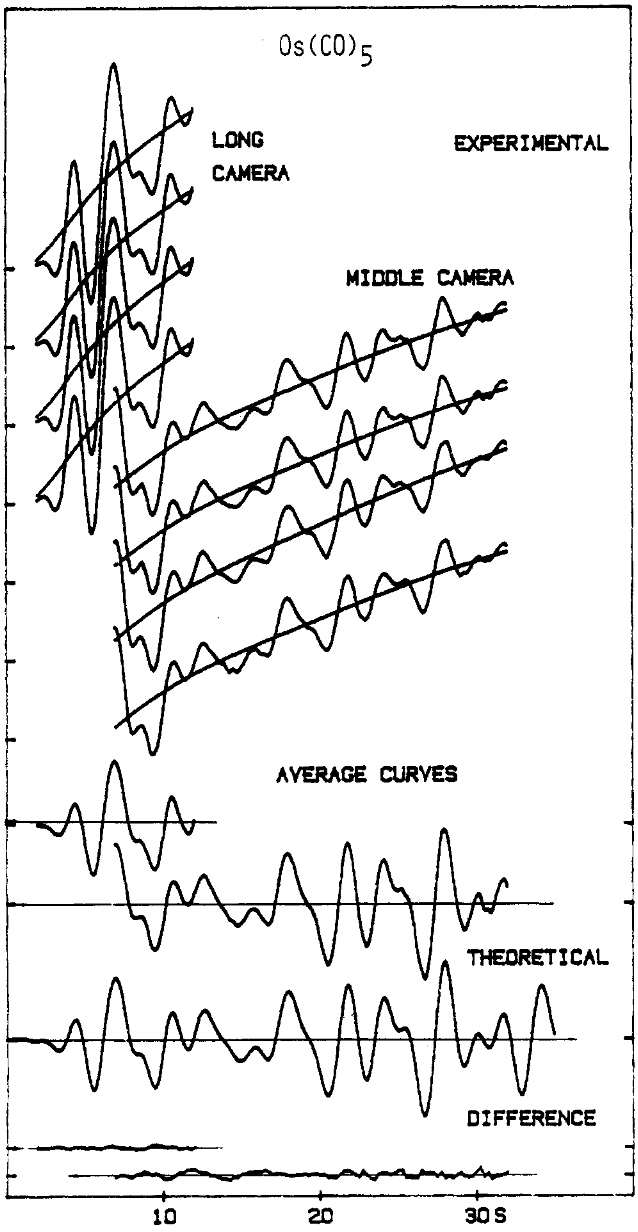

Figure 1. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 10 times relative to the backgrounds. The average curves are $s[s^4I_t - \text{bkgd}]$ minus the contribution from multiple scattering. The difference curves are experimental minus theoretical for model A.

uncertain. An unpublished, but highly accurate, X-ray diffraction study of solid $Fe(CO)_5$ shows the axial and equatorial Fe–C bond distances are equal to within the uncertainty arising from distortion of the equatorial bonds by solid-state packing effects (±0.003 Å).[12]

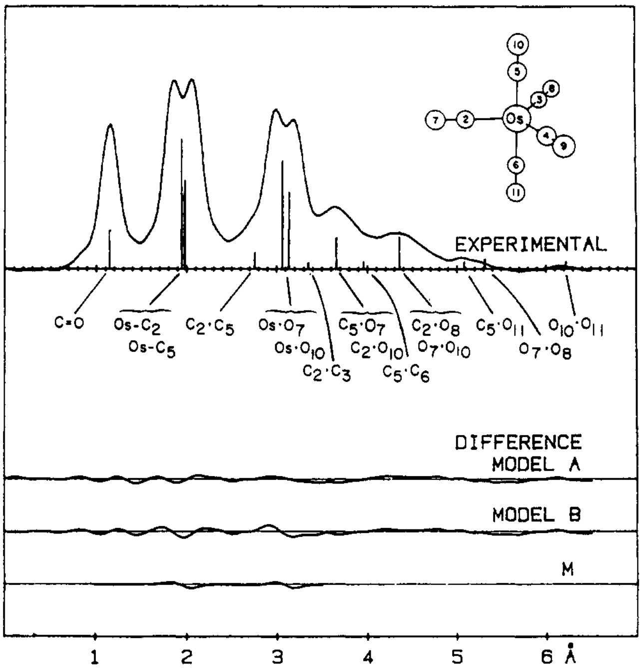

Figure 2. Radial distribution curves. The experimental curve was calculated from a composite of the average curves of Figure 1 with addition of theoretical data from model A for $s < 2.00$ Å^{-1} and with the convergence factor B equal to 0.0025 Å^2. The difference curves for models A and B are experimental minus theoretical; curve M is the contribution from multiple scattering.

Osmium pentacarbonyl was first reported by Hieber and Stallmann in 1943,[13] but its chemistry has received little attention. (The common carbonyl of osmium is $Os_3(CO)_{12}$ which has an extensive chemistry.[14]) Calderazzo and L'Eplattenier carried out some investigations on it in 1967.[15] They suggested that, on the basis of its infrared spectrum, $Os(CO)_5$ was probably trigonal bipyramidal in the gas phase and in heptane solution.[15a] Recent work by us[16] and others[17] has indicated that the chemistry of $Os(CO)_5$ has interesting differences from its much studied congener $Fe(CO)_5$. In view of these studies and the central place of binary metal carbonyls to organometallic chemistry, we have determined the gas-phase structure of $Os(CO)_5$. The question of the difference in the axial and equatorial Os–C bond lengths has also been addressed.

Experimental Section

The sample of $Os(CO)_5$ was prepared at Simon Fraser University by reaction of $Os_3(CO)_{12}$ and CO.[16a] The well-formed crystals melted sharply at 2–2$^1/_2$ °C.

Electron-diffraction photographs were made at room temperature in the Oregon State apparatus under the following conditions: r^3 sector; 8 × 10 in. Kodak projector slide plates (medium contrast) developed in D-19 developer diluted 1:1 for 10 min; nominal nozzle-to-plates distances, 70 and 30 cm (long and intermediate cameras); beam currents, 0.34–0.40 μA; exposure times, 110–170 s; ambient apparatus pressure during exposures, (1.2–3.6) × 10^{-6} Torr; electron wavelength, 0.057 19–0.057 27 Å (calibrated from CO_2: $r(C{=}O) = 1.1646$ Å, $r(O{\cdot}O) = 3.3244$ Å); ranges of data, $2.00 \le s/\text{Å}^{-1} \le 12.00$ (long camera) and $7.00 \le s/\text{Å}^{-1} \le 32.00$ (intermediate cameras); data interval, 0.25 Å^{-1}. Four plates from each of the two camera distances were handled as described previously[18] to yield the total scattering intensity distributions ($s^4(I_t(s))$) from which computer-generated[19] smooth backgrounds were subtracted. The differences multiplied by s ($s = 4\pi\lambda^{-1}$ sin

---

[12] See: Shriver, D. F.; Whitmire, K. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, p 243, ref 18.

[13] Heiber, W.; Stallman, H. *Z. Elektrochem.* **1943**, *49*, 288.

[14] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

[15] (a) Calderazzo, F.; L'Eplattenier, F. *Inorg. Chem.* **1967**, *6*, 1220. (b) L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1967**, *6*, 2092. (c) L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290.

[16] (a) Rushman, P.; van Buuren, G. N.; Shiralian, M. Pomeroy, R. K. *Organometallics* **1983**, *2*, 693. (b) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, *854*. (c) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777. (d) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.*, in press.

[17] For example: (a) Kiel, G.-Y.; Takats, J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1987**, *109*, 2227. (b) Trautman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 2355.

[18] Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

[19] Hedberg, L. "Abstracts", 5th Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1974, p 37.

θ, 2θ is the scattering angle) are the molecular scattering intensities $sI_{\mathrm{m}}(s)$. Curves of the total intensities, the final background, and the averaged molecular intensities are shown in Figure 1. The s^4I_{t} curves, calculated backgrounds, and averaged $sI_{\mathrm{m}}(s)$ curves available as supplementary material.

Structure Analysis

Radial Distribution Curves. Experimental radial distribution curves were calculated in the usual way from the function $I'(s) = sI_{\mathrm{m}}(\mathrm{s})Z_{\mathrm{Os}}Z_{\mathrm{O}}A_{\mathrm{Os}}^{-1}A_{\mathrm{O}}^{-1}\exp(-0.0025s^2)$. The electron scattering amplitudes $f = A/s^2$ as well as the phases η used in later intensity calculations were obtained[20] from new tables.[21] The final curve (in which theoretical data were used for the region $s < 2.00$ Å) is shown in Figure 2. The expected phase-shift effect[22] is evident in the doubled character of the peaks corresponding to the Os–C and Os–O distances. With allowance for the phase shifts, the radial distribution curve was found to be consistent with an $\mathrm{Os(CO)_5}$ molecule of D_{3h} symmetry.

Corrections for Multiple Scattering. Multiple (i.e. three-atom) scattering has been shown to contribute significantly to the electron intensity scattered from gas molecules when the bonds to the central atom are oriented at angles very close to 90°.[23-25] The effect is large for molecules such as $\mathrm{ReF_6}$[23] and $\mathrm{TeF_6}$[24] in which the constituent atoms have large atomic number differences. Even though experience indicates that introduction of multiple scattering corrections affects the values derived for vibrational parameters to a greater extent than it does those of geometrical parameters, we felt it important to check the matter in the case of $\mathrm{Os(CO)_5}$. Of particular concern, of course, was the possible effect of the corrections on the values derived for the axial and equatorial Os–C bonds.

The implementation of multiple scattering corrections depends on the form of the theoretical two-atom molecular intensity function used for the analysis. The formula in use in this laboratory is

$$sI_{\mathrm{m}}(s) = k'\sum_{i\neq j} A_iA_jr_{ij}^{-1}\exp(-l_{ij}^2s^2/2)\cos|\eta_i-\eta_j|\sin[s(r_{ij}-\kappa_{ij}s^2)] \qquad (1)$$

The r's, l's, and κ's are respectively interatomic distances, vibrational amplitudes, and anharmonicity constants; the A's and η's were mentioned above. A suitable approximation of the theoretical three-atom (multiple) scattered intensity has been derived.[26,27] In the slightly modified form necessary for consistency with eq 1 the formula is

$$sI_{\mathrm{MS}}(s) = (a_{\mathrm{O}}'/2)^3k'\sum_{i\neq j\neq k}(s^5/kr_{ij}^2)\mathrm{Re}[if_k^*(s)f_i(s_i)f_j(s_j)] \exp(i\rho s_is_j)J_{\mathrm{O}}[(sr_k)]\exp(-l_{\perp}^2s^2/2) \qquad (2)$$

where a_{O}' is the relativistic Bohr radius, r_k is the perpendicular distance from atom k to r_{ij}, $1_{\perp}^2$ is the mean square amplitude component of atom k perpendicular to r_{ij}, $s_i = sr_j/r_{ij}$, and $s_j = sr_i/r_{ij}$. The meaning of other symbols was defined in the cited articles. We used the following iterative scheme to introduce the multiple scattering corrections.

Trial values of the structural parameters were first obtained by our usual least-squares method[18,28] based on eq 1, fitting a single theoretical curve to the two average intensity curves of Figure 1. These parameter values were then used to calculate the multiple scattering intensity according to eq 2. (Only those triplets containing osmium were included in the calculation since terms without osmium have relatively low weight). The multiple scattering thus calculated was subtracted from the average experimental intensity curves to obtain "corrected" versions of these curves and the structure again adjusted by least squares. The process converged after a few iterations. The quality of fit was substantially improved by the introduction of the multiple scattering corrections, but as will be discussed later, the measured structure is similar to that obtained without them.

Structure Refinement. The effects of vibrational averaging were expected to be important in $\mathrm{Os(CO)_5}$, and we elected to carry out the refinement of the structure in terms of the geometrically consistent r_α-type distance. The centrifugal distortions (δr), perpendicular amplitude corrections (K), and mean square amplitudes (l^2) that comprise the necessary corrections to r_{a} ($r_{\mathrm{a}} - r_\alpha = \delta r + K - l^2/r$) were calculated from a rough quadratic force field. Since the corrections are usually not very sensitive to force-field differences and since only two IR-active frequencies ($\mathrm{C{\equiv}O}$ stretches) for $\mathrm{Os(CO)_5}$ have been assigned,[15a] we used the force field for $\mathrm{Fe(CO)_5}$[11] for this purpose. Following tests that ruled out C_{4v} as a possible symmetry for the molecule, we based our refinements on assumed molecular symmetry D_{3h}. The parameters were $\langle r(\mathrm{Os{-}C})\rangle = [2r(\mathrm{Os{-}C})_{\mathrm{ax}} + 3r(\mathrm{Os{-}C})_{\mathrm{eq}}]/5$, $\Delta r(\mathrm{Os{-}C}) = r(\mathrm{Os{-}C})_{\mathrm{ax}} - r(\mathrm{Os{-}C})_{\mathrm{eq}}$, and $\langle r(\mathrm{C{\equiv}O})\rangle$ and $\Delta r(\mathrm{C{\equiv}O})$ similarly defined. There are also 16 vibrational amplitude parameters.

The value of the parameter $\Delta r(\mathrm{Os{-}C})$ is one of the most interesting structural quantities, but its determination turned out to be very difficult due to large correlations with other parameters. We expected, and found, that $\Delta r(\mathrm{Os{-}C})$, $l(\mathrm{Os{-}C})_{\mathrm{ax}}$, and $l(\mathrm{Os{-}C})_{\mathrm{eq}}$, as well as $\Delta r(\mathrm{C{\equiv}O})$, $l(\mathrm{C{\equiv}O})_{\mathrm{ax}}$, and $l(\mathrm{C{\equiv}O})_{\mathrm{eq}}$ could not be refined simultaneously. A common approach in such cases is to investigate the quality of the fits, as measured by magnitudes of the R factor, obtained from refinements that incorporate assumptions about the values of the correlated parameters. Accordingly, we carried out a series of refinements, with and without corrections for multiple scattering, in which $\Delta r(\mathrm{C{\equiv}O})$ and certain amplitude differences (axial minus equatorial) were assigned values over plausible ranges. These ranges were $-0.02 \leq \Delta r(\mathrm{C{\equiv}O})/\text{Å} \leq +0.02$, $-0.010 \leq \Delta l(\mathrm{Os{-}C})/\text{Å} \leq +0.007$, $-0.002 \leq \Delta l(\mathrm{C{\equiv}O})/\text{Å} \leq +0.002$, and $-0.010 \leq \Delta l(\mathrm{Os{\cdot}O})/\text{Å} \leq +0.007$. It was necessary to refine some of the remaining amplitudes in groups (amplitude differences within groups were taken from calculated values). A few of the amplitudes for the longest distances tended to refine to unreasonable values and were assigned values suggested by the calculated ones. Some corrections for vibrational anharmonicity, estimated by the usual diatomic approximation,[29] were also included: values of κ ($\times 10^6$) for the Os—C, C≡O, and Os·O distances were respectively 1.6, 0.90, and 2.0. Anharmonicities of other distances were ignored.

Results. Investigation of the parameter space described above led to results from some two dozen converged refinements. Conclusions drawn from examination of these refinements are as follows. (1) Refinements with and without corrections for multiple scattering, but otherwise

---

(20) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 1003.

(21) Ross, A. W.; Fink, M.; Hilderbrandt, R., to be submitted for publication.

(22) Schomaker, V.; Glauber, R. J. *Nature (London)* **1952**, *170*, 291.

(23) Jacob, E. J.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 2231.

(24) Gundersen, G.; Hedberg, K.; Strand, T. G. *J. Chem. Phys.* **1978**, *68*, 3548.

(25) Miller, B. R.; Fink, M. *J. Chem. Phys.* **1981**, *75*, 5326.

(26) Bartell, L. S. *J. Chem. Phys.* **1975**, *63*, 3750.

(27) Miller, B. R.; Bartell, L. S. *J. Chem. Phys.* **1980**, *72*, 800.

(28) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.

(29) Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 505.

Table I. Structural Results for Osmium Pentacarbonyl[a,b]

	model A[c]				model B[d]	
parameters	r_α	r_g[e]	r_a	l	r_α	l
$\langle r(\mathrm{C{\equiv}O})\rangle$	1.130 (4)	1.142	1.140	0.043 (4)	1.130 (5)	0.043 (4)
$\Delta r(\mathrm{C{\equiv}O})$	[0]	[0]	[0]		[0]	
$\langle r(\mathrm{Os{-}C})\rangle$	1.955 (4)	1.962	1.961		1.956 (5)	
$\Delta r(\mathrm{Os{-}C})$	0.045 (46)	0.047	0.048		0.053 (40)	
$\mathrm{Os{-}C_{eq}}$	1.937 (19)	1.943	1.942	0.049 }(9)	1.935 (16)	0.046 }(11)
$\mathrm{Os{-}C_{ax}}$	1.982 (20)	1.990	1.989	0.046	1.988 (25)	0.043
$\mathrm{C_2{\cdot}C_5}$	2.772 (9)	2.779	2.773	0.11 (25)	2.774 (9)	0.123 (28)
$\mathrm{Os{\cdot}O_{eq}}$	3.068 (35)	3.078	3.077	0.051 }(9)	3.065 (32)	0.047 }(11)
$\mathrm{Os{\cdot}O_{ax}}$	3.112 (52)	3.127	3.126	0.048	3.118 (45)	0.044
$\mathrm{C_2{\cdot}C_3}$	3.356 (33)	3.360	3.359	0.077 (31)	3.351 (28)	0.066 (29)
$\mathrm{C_5{\cdot}O_7}$	3.652 (36)	3.662	3.656	0.149 }(19)	3.653 (32)	0.150 }(22)
$\mathrm{C_2{\cdot}O_{10}}$	3.666 (48)	3.678	3.671	0.161	3.669 (42)	0.162
$\mathrm{C_5{\cdot}C_6}$	3.964 (56)	3.968	3.967	[0.066]	3.975 (49)	[0.066]
$\mathrm{C_2{\cdot}O_8}$	4.371 (34)	4.378	4.365	0.239 }(57)	4.366 (30)	0.234 }(61)
$\mathrm{O_7{\cdot}O_{10}}$	4.370 (15)	4.382	4.363	0.283	4.372 (14)	0.278
$\mathrm{C_5{\cdot}O_{11}}$	5.094 (52)	5.100	5.098	[0.100]	5.105 (46)	[0.100]
$\mathrm{O_7{\cdot}O_8}$	5.313 (61)	5.320	5.313	[0.200]	5.308 (55)	[0.200]
$\mathrm{O_{10}{\cdot}O_{11}}$	6.224 (104)	6.231	6.229	[0.100]	6.235 (91)	[0.100]
R[f]	0.0857				0.0965	

[a] D_{3h} symmetry. Distances (r) and amplitudes (l) in angstroms. Quantities in parentheses are estimated 2σ. For definitions see text. [b] The first four parameters were used to define the geometry. [c] Multiple scattering corrections included. [d] Multiple scattering corrections not included. [e] Uncertainties estimated to be the same as for r_α. [f] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\mathrm{obsd}))^2]^{1/2}$, where $\Delta_i = s_i I_i(\mathrm{obsd}) - s_i I_i(\mathrm{calcd})$.

Table II. Osmium Pentacarbonyl: Correlation Matrix (×100) for Parameters of Model A[a]

	parameter	σ[b]	$\langle r_1\rangle$	Δr_2	$\langle r_3\rangle$	l_4	l_5	l_6	l_7	l_8	l_9	l_{10}
1	$\langle r(\mathrm{Os{-}C})\rangle$	0.0058	100	60	−39	−7	−60	−3	−60	1	2	−8
2	$\Delta r(\mathrm{Os{-}C})$	1.09		100	−16	−2	−98	−12	−98	4	6	−11
3	$\langle r(\mathrm{C{\equiv}O})\rangle$	0.059			100	−1	16	4	16	−4	−8	2
4	$l(\mathrm{C{\equiv}O})$	0.108				100	12	−8	9	−5	10	2
5	$l(\mathrm{Os{-}C_{eq}})$	0.32					100	10	98	−5	−3	11
6	$l(\mathrm{C_2{\cdot}C_5})$	0.85						100	12	−1	7	−5
7	$l(\mathrm{Os{\cdot}O_{eq}})$	0.32							100	2	−2	11
8	$l(\mathrm{C_2{\cdot}C_3})$	0.109								100	26	−6
9	$l(\mathrm{C_5{\cdot}O_7})$	0.65									100	−26
10	$l(\mathrm{C_2{\cdot}O_8})$	1.96										100

[a] Distances (r) and amplitudes (l) in angstroms. For numbering of atoms see Figure 2. For explanation about grouping of amplitudes see text. [b] Standard deviations (×100) from least squares.

based on similar assumptions, gave similar values for corresponding distances and amplitudes. The quality of the fits to the experimental intensity, however, was significantly (i.e. 10–12%) better when the multiple scattering corrections were included. (2) Within each class of refinement (those with and without multiple scattering corrections), the qualities of fit were similar over most of the parameter space designated above. There is thus no basis in the diffraction data for decisions about relative magnitudes of the parameters involved in the assumptions. (3) The values of $\langle r(\mathrm{Os{-}C})\rangle$ and $\langle r(\mathrm{C{\equiv}O})\rangle$ were essentially invariant to the assumptions. They may thus be regarded as accurately determined. (4) The value of $\Delta r(\mathrm{Os{-}C})$ tends to be positive (longer axial bonds) over nearly all of the parameter space investigated. However, with $\Delta l(\mathrm{Os{-}C}) \geq +0.006$, $\Delta r(\mathrm{Os{-}C})$ becomes insignificantly different from zero. Further, $\Delta r(\mathrm{Os{-}C})$ seems not to be very sensitive to the other assumptions.

The second and fourth of these observations make it difficult to select a single "best model". The parameter values of model A in Table I, a model that includes multiple scattering corrections, are representative of one of the best fits. Because other models that gave nearly as good fits had slightly different parameter values, the uncertainties for the parameters of model A as originally calculated were unrealistic. Accordingly, we have increased the calculated uncertainties for the geometrical parameters of this model to reflect additional uncertainties deriving from the other results. Our method, found to be satisfactory in other cases, was to set all variables to the values found for model A and to carry out one cycle of refinement in which all were released but allowed zero shifts. The parameters and uncertainties for model B, which does not contain multiple scattering corrections but was obtained under refinement conditions identical to model A, are also found in Table I. Table II is the correlation matrix for model A. The theoretical intensity curve for it is seen in Figure 1, and the agreement of the two models with the experimental radial distribution is seen in Figure 2.

Discussion

As expected, the electron-diffraction data for $\mathrm{Os(CO)_5}$ were found to be consistent with a molecule of D_{3h} symmetry. The mean C≡O bond length in $\mathrm{Os(CO)_5}$ ($r_g = 1.142$ (2) Å) is similar to the r_g values in other transition-metal carbonyls; examples are $\mathrm{V(CO)_6}$, 1.138 (2) Å,[30] $\mathrm{Mo(CO)_6}$, 1.148 (3) Å,[31] $\mathrm{W(CO)_6}$, 1.145 (2) Å,[31] $\mathrm{Fe(CO)_5}$, 1.147 (2) Å,[6-9] and $\mathrm{Ni(CO)_4}$, 1.141 (2) Å.[32] Since corrections for thermal motion were not made in the crystallographic work on $\mathrm{Os_3(CO)_{12}}$,[33] the more appropriate distance type for comparison purposes from the gas-phase work is r_α. Our average value for $r_\alpha(\mathrm{C{\equiv}O})$ (1.130 (4) Å) is slightly shorter than that in $\mathrm{Os_3(CO)_{12}}$ (1.140 (8) Å), but the difference is of doubtful significance. On the other hand, our gas-phase

---

(30) Schmidling, D. G. *J. Mol. Struct.* **1975**, *24*, 1.

(31) Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *1*, 2711.

(32) Hedberg, L.; Iijima, T.; Hedberg, K. *J. Chem. Phys.* **1979**, *70*, 3224.

(33) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878. (b) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962**, *1*, 521.

value for the mean Os–C bond length, r_α = 1.955 (4) Å, is somewhat longer than the crystallographic values of 1.946 (6) (axial) and 1.912 (7) Å (equatorial) for $Os_3(CO)_{12}$. Recent theoretical values are 1.99 and 1.98 Å for the equatorial and axial distances, respectively.[34] Some experimental Os–C distances (in angstroms) from X-ray crystallographic studies of derivatives of $Os(CO)_5$ are 1.926 (6) and 1.911 (7) for equatorial bonds and 1.952 (6) and 1.939 (6) for axial bonds in eq-$Os(CO)_4(SbPh_3)$;[16c] 1.916 (2) and 1.925 (8) (equatorial) and 1.937 (7) and 1.955 (7) (axial) in eq-$Os(CO)_4[C_2(SiMe_3)_2]$,[35] a range of 1.917 (6)–1.967 (6) in $[Os_2(CO)_8]^{2-}$,[36] and a range of 1.81 (3)–1.98 (3) with a mean of 1.89 in $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$[16b] (15 crystallographically independent Os–C bond lengths for the $Os(CO)_5$ unit). All these values are less than the sum of the Pauling covalent single-bond radii for Os and C (2.01 Å) and suggest that the bonds have some multiple-bond character.

Perhaps the most interesting structural feature of $Os(CO)_5$ is the relative length of the two types of Os–C bonds. Unfortunately, our data do not permit an unequivocal determination of the matter because of the high correlations among these and other parameters that affect the results. Our study of the effects of these correlated parameters on the parameter Δr(Os–C), however, showed that most combinations of them led to an axial Os–C bond longer than the equatorial. A few such combinations were discovered that led to essentially no difference in the lengths of these bonds. It is our judgement that the weight of our evidence points toward an axial bond longer than the equatorial one by a few hundredths of an angstrom.

Although inclusion of corrections for multiple scattering in $Os(CO)_5$ significantly improved the fit to experiment, the improvement has very little effect on the parameter values, as may be seen from comparison of the results for the two models in Table I. This result differs from that obtained for TeF_6[24] where a substantial increase (ca. 10%) in some of the vibrational amplitude values accompanied introduction of corrections. It is, however, consistent with the smaller role played by multiple scattering in trigonal-bipyramidal molecules than in octahedral molecules. The contributions to multiple scattering are largely from triplets of atoms at 90° that include the central atom. There are 72 of these vs 6 atomic pairs that include the central atom in octahedral molecules and 48 triplets vs 10 pairs in $Os(CO)_5$. In TeF_6 the corrections lowered the R factor about 60% whereas in $Os(CO)_5$ the lowering is about 12%. The improvement in fit afforded by the corrections in $Os(CO)_5$ may be seen in the intensity and radial distribution difference curves for models A and B in Figures 1 and 2. Curve M in Figure 2 shows the contribution of multiple scattering to the radial distribution; it was obtained by Fourier transformation of the calculated multiple scattering intensity.

Although our final results for $Os(CO)_5$ are based on use of the latest set[21] of atomic scattering factors for electrons, we also tested the earlier set[37] that has been widely used for the past several years. Slightly better agreement with experiment was obtained from the newer set, but the structures derived for $Os(CO)_5$ were essentially identical.

Acknowledgment. This work was supported by the National Science Foundation under Grant 84-11165 to Oregon State University. We thank Dr. P. Rushman and Mr. H. B. Davis for providing the sample of $Os(CO)_5$.

Supplementary Material Available: Tables of the total scattered intensities $s^4I_t(s)$, the calculated backgrounds from each plate, the averaged molecular intensities $sI_m(s)$ from each camera distance, and the calculated multiple scattering (10 pages). Ordering information is given on any current masthead page.

---

[34] Ziegler, T.; Tschinke, V.; Ursen, C. *J. Am. Chem. Soc.* **1987**, *109*, 4825.

[35] Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 191.

[36] Hsu, L.-Y.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1985**, *4*, 1483.

[37] Schafer, L.; Yates, A.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.