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Infrared Spectrum of Osmium Tetracarbonyl Trimer, $Os_3(CO)_{12}$; Assignment of CO and MC Stretching Absorptions[1]

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The infrared spectrum of $Os_3(CO)_{12}$ in the region 3000–290 cm.$^{-1}$ is reported. Using the simplified secular equations of Cotton and Kraihanzel, an assignment of the four carbonyl stretching absorptions is proposed based to a first approximation on the relative bond orders expected for each of the two different kinds of carbonyl groups and on the interactions between them. However, because of the relative intensities of the absorptions, it seems likely that axial and radial modes are not as well separated as in the group theoretical treatment. The metal–carbon stretching modes are tentatively assigned by comparison with spectra of structurally related derivatives to bands in the region 500–400 cm.$^{-1}$.

Introduction

The report of a trimeric tetracarbonyl of rhenium[2] has turned our attention to the spectrum of $Os_3(CO)_{12}$, a trimer of known structure.[3] Brief mention of its spectrum has appeared twice thus far. The first[4] is a report of absorptions in the carbonyl stretching region but appears to contain extraneous bands. The second[5] is a report of four bands each for the carbonyl and metal–carbon stretching modes in tabular form with data for a number of other metal carbonyl derivatives to illustrate a proposed rule for selection of the low-energy absorptions. Without an accompanying figure of the spectrum, these data are inadequate for purposes of comparison with spectra of new and possibly structurally related molecules, such as the one discovered for rhenium.[2] We have therefore repeated the preparation of $Os_3(CO)_{12}$ and wish here to report its infrared spectrum in the region 3000–290 cm.$^{-1}$. A vibrational analysis of the carbonyl stretching modes is also presented.

Experimental

The preparation of crude $Os_3(CO)_{12}$ was carried out as reported by Hieber and Stallmann,[6] for the compound they then believed to be the enneacarbonyl. Sublimation of the product is not sufficient to obtain pure sample, which must be recrystallized from cyclohexane. We have monitored the purity of the sample by infrared, which compared well with that of the center fraction of a sample further purified by elution chromatography (silica gel support, cyclohexane solvent).

The principal absorptions in the entire region 4000 to 700 cm.$^{-1}$ were the carbonyl stretching modes and are shown in Figure 1. The maxima were measured[7] to be at 2068 (s), 2034.5 (s), 2014 (m), and 2002 (m) cm.$^{-1}$. In the lower energy region, scanned with a Beckman IR-5A equipped with a CsBr prism, a number of principal bands were observed. These are shown in Figure 2; the positions of the band maxima were measured to be at 606 (s), 586 (s), 565 (m), 535 (w), 498 (s), 477 (m), 466 (s), 447 (sh, w), 432 (w), and 413 (s) cm.$^{-1}$.

Discussion

Vibrational Analysis.—$Os_3(CO)_{12}$ belongs to the point group D_{3h},[3] whose structure and internal symmetry coordinates for the carbonyl bond stretching motions are shown in Figure 3. A vibrational analysis has been carried out from symmetry properties and group theory, and the results and summarized in Table I. The carbonyl stretching modes are constructed from the internal coordinates by the methods illustrated by Wilson, Decius, and Cross.[8] Those for the axial carbonyl groups are constructed in a straightforward manner and are listed in Table II. The symmetry coordinates for the radial carbonyls, however, present a somewhat more involved calculation because there are two vibrations of species e′. This is a case where $n^{(\gamma)} > 1$, in the

Table I

Number and Representation of the Expected Infrared Active Vibrations of $Os_3(CO)_{12}$, D_{3h} Point Group

	Number of modes			
Species	Total	Skeletal	C≡O stretch	C≡O def.
a_2''	6	3	1[a]	2
e'	15	8	3[b]	4

[a] Axial. [b] One axial, two radial modes.

Table II

Internal Symmetry Coordinates for C≡O Stretching Modes, $Os_3(CO)_{12}$, D_{3h} Point Group

$$S^{(e')}_{\text{axial}} = \frac{1}{2\sqrt{3}}(2r_{13} + 2r_{14} - r_{23} - r_{24} - r_{33} - r_{34})$$

$$S^{(a_2)}_{\text{axial}} = \frac{1}{\sqrt{6}}(r_{13} + r_{23} + r_{33} - r_{14} - r_{24} - r_{34})$$

$$S^{(e')}_{a_1\,\text{radial}} = \frac{1}{2\sqrt{3}}(2r_{11} + 2r_{12} - r_{21} - r_{22} - r_{31} - r_{32})$$

$$S^{(e')}_{b_2\,\text{radial}} = \frac{1}{2}(r_{21} - r_{22} - r_{31} + r_{32})$$

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[1] This work has been supported by Grant No. GP 1696 from the National Science Foundation.

[2] (a) H. D. Kaesz, W. Fellmann, D. K. Huggins, and J. M. Smith, Paper No. 28, Symposium on Metal Carbonyls and Related Complexes, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964; (b) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

[3] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

[4] W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

[5] H. P. Fritz and E. F. Paulus, *Z. Naturforsch.*, **18b**, 435 (1963).

[6] W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).

[7] The spectrum was calibrated against the 1847.8 cm.$^{-1}$ water vapor absorption; *cf.* Band No. 50, Table 5, E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Natl. Bur. Std.*, **64A**, 1 (1960).

[8] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 117–125.

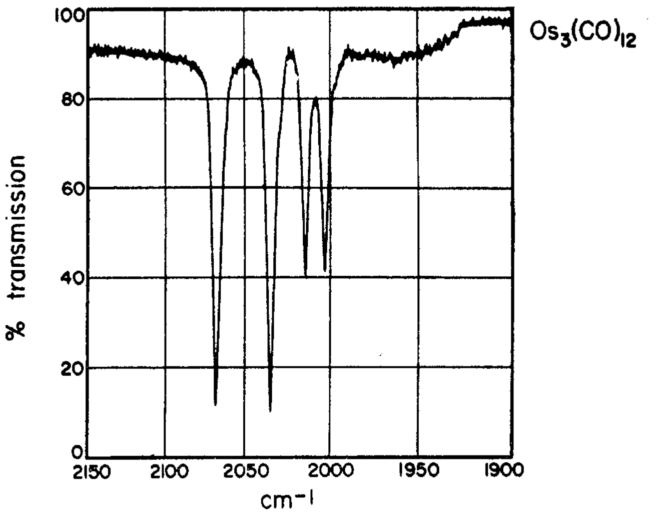


Figure 1.—High resolution infrared spectrum of $Os_3(CO)_{12}$, Beckman IR-4, LiF prism, cyclohexane solution, 0.8 mg./ml. (10^{-6} mole/ml.).

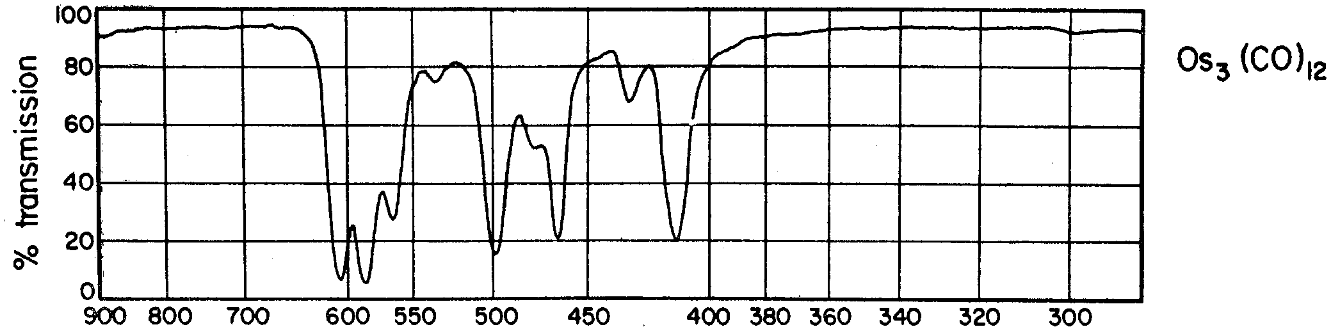


Figure 2.—Infrared spectrum of $Os_3(CO)_{12}$, Beckman IR-5A, CsBr prism, KBr pellet, approximately 2.3 mg./100 mg. concentration.

notation of Wilson, Decius, and Cross,[8] and is treated according to the method outlined on pp. 135–140 of that reference. The present discussion is simplified since we are dealing with a molecule of the same symmetry as that in the example chosen in that reference.[8]

The internal coordinates of the six radial carbonyls may be grouped into three sets each consisting of two internal coordinates having a common central metal atom. The operations of the point group D_{3h} can be divided into two groups, those which merely permute each set of two within itself, and those which send each set as a rigid unit into another set of two. The operations which merely permute each set within itself all belong to the subgroup C_{2v} of the point group D_{3h}. Reorganized internal symmetry coordinates, $K_i^{(\nu)}$, were constructed under C_{2v} for each of the three sets of two internal coordinates (where the subscript refers to the metal atom).

$$K_i^{(a_1)} = \frac{1}{\sqrt{2}}(r_{i1} + r_{i2})$$

$$K_i^{(a_2)} = 0$$

$$K_i^{(b_1)} = 0$$

$$K_i^{(b_2)} = \frac{1}{\sqrt{2}}(r_{i1} - r_{i2})$$

The symmetry operations under D_{3h} which send metal atom M_1 into metal atom M_2, now send $K_1^{(a_1)}$ into $K_2^{(a_1)}$, etc. The final symmetry coordinates under D_{3h} are constructed by treating the $K_i^{(a_1)}$, $K_i^{(a_2)}$, $K_i^{(b_1)}$, and $K_i^{(b_2)}$ families separately.

According to the correlation tables for D_{3h} (ref. 8, p. 336), e′ under D_{3h} is composed of a_1 and b_2 under C_{2v}. One of the two internal symmetry coordinates of the radial groups of species e′ is composed of one or more reorganized coordinates from the family $K_i^{(a_1)}$. This is designated $S^{(e')}_{a_1\,\mathrm{radial}}$, and is listed in Table II; it was obtained by operating directly on $K_1^{(a_1)}$ under D_{3h}. The second internal symmetry coordinate for the e′ species is composed of one or more reorganized coordinates from the family $K_i^{(b_2)}$. However, as explained for the case for cyclopropane (ref. 8, p. 138), the reorganized internal symmetry coordinate $K_1^{(b_2)}$ is not correctly oriented for construction of the degenerate symmetry coordinate $S^{(e')}_{b_2\,\mathrm{radial}}$. By operating on $K_2^{(b_2)}$ according to the characters of a_1 under C_{2v}, a correct combination of the reorganized coordinates is obtained, namely $[K_2^{(b_2)} - K_3^{(b_2)}]$. From this combination, the symmetry coordinate $S^{(e')}_{b_2\,\mathrm{radial}}$ is obtained and is listed on the last line of Table II. All the symmetry coordinates are shown in Figure 4.

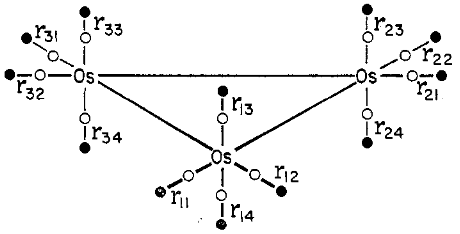


Figure 3.—Structure and internal coordinates of carbonyl groups for $Os_3(CO)_{12}$; O represents carbon atoms, ● represents oxygen atoms.

Assignment of Carbonyl Modes.—In agreement with vibrational analysis, four principal carbonyl stretching bands are observed for $Os_3(CO)_{12}$ (Figure 1). To a first approximation, the carbonyl absorptions may be grouped into two pairs, those of the carbonyls opposite a substituent (the radial carbonyls opposite the metal–metal bonds) and those opposite each other (the axial carbonyls). This separation is based on the difference in bond order due to π-bonding effects in the two kinds of carbonyl groups. We assume that those opposite each other will have to compete equally for the same

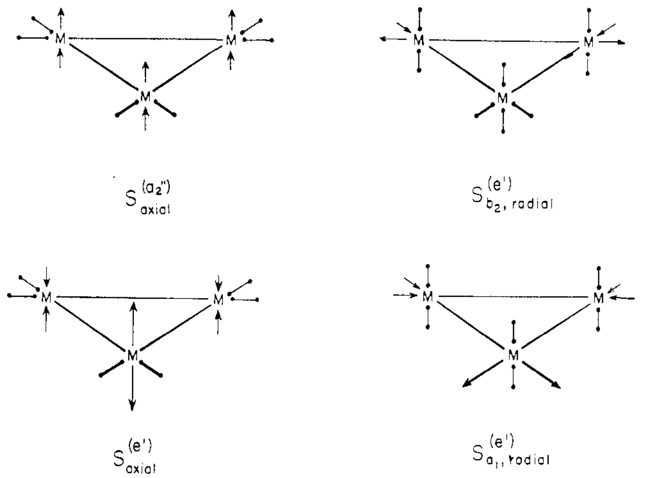
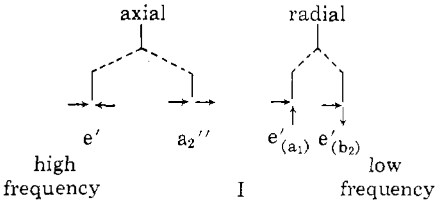


Figure 4.—Relative orientation of internal coordinates for carbonyl bond stretching modes in the infrared active species D_{3h} point group for $Os_3(CO)_{12}$.

π-electrons and will have slightly higher CO bond order than each of the carbonyl groups opposite a metal–metal bond, since the metal atom as a substituent seems to be a weaker π-acceptor than the carbonyl group. The only real evidence thus far to support this comes from analysis of other polynuclear carbonyls, $M_2(CO)_{10}$, M = Tc or Re,[9] whose spectra can satisfactorily be assigned on this basis. (The relative intensity of the three bands in the carbonyls of Tc and Re suggests an assignment similar to those for spectra of structurally related derivatives, $XM(CO)_5$,[10] where there is less question about the relative π-donor ability of the ligand compared to the carbonyl group.) We therefore would expect the radial modes to be centered around a lower energy than the axial modes. Each of these modes is split into a pair primarily due to the coupling within each local $[M(CO)_4]$ unit. In the mode where the oscillating dipoles due to carbonyl vibrations are opposing each other, these will be of higher energy than when they are pointing in the same direction[10] (*i.e.*, the coupling constant between the carbonyl group stretching motions is positive). Such an assignment is illustrated in diagram I. However, if the separation arising from the difference in CO bond order is not very great, then it is possible that the assignment of the two middle bands will be reversed, as shown in diagram II.



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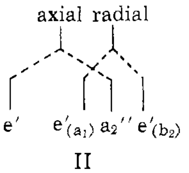

II

In an extreme case, one might conceive that the two radial modes might be placed in between the two axial modes, not shown schematically here. One may resolve this problem in the assignment through a calculation of approximate force constants according to the method of Cotton and Kraihanzel.[11]

To do this, we must assume that the interaction of carbonyl groups across the metal–metal bond is negligible. In that case, the factored secular equations for the carbonyl modes in the trimer would be identical with those given by Cotton and Kraihanzel for monomeric *cis*-tetracarbonyl derivatives. This can easily be verified by inspection of the carbonyl modes; the relative motions of the carbonyl groups within each of the $M(CO)_4$ units in the four active modes of the trimer (Figure 4) are identical with the corresponding modes for the monomeric derivatives.[12] (The modes of the monomeric *cis*-tetracarbonyl derivatives can be correlated with those of the trimer as follows: axial modes, species a_1 and b_1 (C_{2v}) with e′ and a_2'' (D_{3h}), and radial modes, species a_1 and b_2 (C_{2v}) with each of the related e′ species (D_{3h}), respectively.) The factored secular equations may be used to calculate *approximate* force constants. All four bands are well resolved and their frequencies equally reliable, so the graphical method of Cotton[11c] was used in choosing the best assignment. This in fact turned out to be the one shown in diagram I; this one alone produced acceptable force constants. The graphical solution resembled the one shown for assignment 3 for $[Mn(CO)_4Cl]_2$ (in Table IX and Figure 3-3) of ref. 11c. The present assignment is summarized in Table III. For the sake of completion, we tried several other likely and unlikely permutations of the frequencies and found all of these unacceptable because of the solutions they give, similar to the rejected assignments in the work on the tetracarbonyl halide dimers.[11c]

Table III

Assignments, Approximate Force Constants, and Calculated Frequencies for the Carbonyl Stretching Absorptions in $Os_3(CO)_{12}$

Obsd., cm.$^{-1}$	Species[a]	Calcd., cm.$^{-1}$	Force constants[b]
2068	e′ axial	2068	k_1 = 16.32
2035	a_2'' axial	2035	k_2 = 16.96
2014	e′ (a_1 radial)	2013	k_i = 0.12
2002	e′ (b_2 radial)	2003	

[a] See Figure 4 and Table II for a description of these modes. [b] mdynes/Å.

However, while the acceptable assignment is analogous to that in structurally related molecules (the tetracarbonyl halide dimers), the intensity relationships between the bands are significantly different in the two types of spectra. In the tetracarbonyl halide dimers,

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(9) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

(10) (a) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962); (b) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(11) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); (c) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(12) R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962).

the bands are[13] (starting at the highest frequency) A, weak; B, strong; C, weak (or medium); and D, strong. In the present spectrum (Figure 1), the bands (in the same order) appear strong, strong, weak, and weak. We believe the difference in the appearance is mainly due to coupling between the radial and axial modes of the same symmetry species, accompanied by exchange of intensity between them. In particular, transfer of intensity from the highest lying to the lowest lying bands (2068 and 2002 cm.$^{-1}$, assigned as the $e'_{(\text{axial})}$ and $e'_{(b_2\ \text{radial})}$, respectively) in the present spectrum, would convert it to the more familiar pattern observed for the tetracarbonyl halide dimers. This hypothetical transfer of intensity would also be accompanied by an increase in the separation in the two bands, also observed in the tetracarbonyl halide dimers. We may therefore assume that the axial and radial motions are not as well separated in the present derivatives as they are in the former ones. This is reminiscent of the similar behavior from similar relative intensity considerations in the spectrum of $Mn_2(CO)_{10}$, on the one hand, compared to those of $Re_2(CO)_{10}$, $Tc_2(CO)_{10}$, and structurally related derivatives, on the other.[9]

Low-Energy Region.—From vibrational analysis we expect ten bands for the metal–carbon stretching and the carbonyl deformation vibrations (Table I). From previous assignments[14] these are expected in the region 700–400 cm.$^{-1}$; we have observed nine or ten bands in that region (Figure 2) but the agreement is possibly fortuitous. Some of the weaker bands may be combination modes or overtones and with improved resolution or greatly increased sample intensity a larger number of maxima might be counted.

From analysis of the carbonyl stretching region, it is a simple matter to arrive at the metal carbon stretching modes; the internal coordinates of the two vibrations are transformed identically under the symmetry operations of the group. We therefore expect four absorptions arising from the metal–carbon stretching modes, and we propose that bands composed principally of that motion are to be found near 400 cm.$^{-1}$, such as any four of the bands between 400 and 500 cm.$^{-1}$. This is somewhat in conflict with the assignment of Fritz and Paulus,[5] who propose four bands in the region 500–571 cm.$^{-1}$ based on a sum rule for the metal–carbon and carbonyl stretching frequencies. There is experimental evidence on structurally related derivatives[15] (in addition to previous normal coordinate analyses of metal carbonyls[14]) to support our choice of the lower absorptions.

In the derivatives $[M(CO)_4X]_2$, $X = Cl$, Br, or I, $M = Mn$, Tc, or Re, changing the halogen atom (from Cl to I) causes a shift to higher energy of the average of the absorptions near 400–450 cm.$^{-1}$,[15a] which is in exactly the opposite direction for the shift on the carbonyl stretching absorptions.[13] This is what would be expected from metal–carbon vibrations (following the expected inverse effect on bond order of substituents on these two bonds).[16] By comparison, the bands in the region 550 cm.$^{-1}$ and above are observed to shift very little or not at all with these substitutions. Substitution of metal atom (from Mn to Re) keeping the halogen constant in these derivatives, however, will produce a shift in both sets of bands, but a greater shift in the lower-lying set. (A shift of 75 cm.$^{-1}$, from 415 to 340 cm.$^{-1}$, is observed for the average of the lower-lying bands while one of 40 cm.$^{-1}$, from 630 to 590 cm.$^{-1}$, is observed for higher-lying bands, in going from the derivatives of manganese to those of rhenium.[15a]) This indicates that metal–carbon stretching motions are concentrated more in the lower than in the higher lying bands of the low-energy region.

The relative positions of the metal–carbon modes will be different from those for the analogous carbonyl vibrations. For the carbonyls, we have assumed that the bond order in the axial groups will be higher than in the radial groups; the inverse will then be true for the analogous metal–carbon bond orders. We would therefore expect a pair of bands, the radial modes, closely spaced (due to *cis* coupling) followed at *lower* energy by a pair of bands, the axial modes, more widely spaced (*trans* coupling), *i.e.*, the assignment $e'_{(a_1\ \text{radial})} > e'_{(b_2\ \text{radial})} > e'_{(\text{axial})} > a_2''_{(\text{axial})}$ in order of decreasing energy. Due to the possibility of exchange of intensities between the radial and axial modes of the same symmetry species (in the first three modes listed), it is a little difficult to assign the bands from the intensity pattern alone. However, from the expected spacing due to coupling, one could make the above-mentioned assignment to the set of bands 477, 466, 432, and 413 cm.$^{-1}$, or possibly to the set of bands 498, 477, 466, and 413 cm.$^{-1}$, in that order, respectively. Conceivably, the two middle modes might be reversed in order (as in case II for the carbonyls mentioned above), however if the axial and radial modes were appreciably mixed in the e' symmetry species, this would have no physical significance.

It is not possible short of a normal coordinate analysis to test these assignments by some quantitative method. We have attempted to calculate approximate force constants similar to those for the carbonyl modes above, but the necessary simplifications in the secular equations (due to insufficient data at this time) have resulted in entirely unacceptable results. The approximation of factoring out other modes and their interactions is obviously untenable for the low-energy modes. The force constants are about 40% lower than what we would expect for these vibrations,[14] although they are in the appropriate *relative* magnitude (which they would be in any case because of our initial assumptions).

Acknowledgment.—We are grateful for the assistance of Dr. W. Fellmann of these laboratories in the preparation and purification of some of the samples of $Os_3(CO)_{12}$.

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(13) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(14) (a) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963); (b) R. S. McDowell, W. D. Horrocks, Jr., and J. D. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

(15) (a) N. Flitcroft and H. D. Kaesz, unpublished observations; (b) D. M. Adams, *J. Chem. Soc.*, 1771 (1964).

(16) (a) L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962); (b) M. Bigorgne and A. Zelwer, *Bull. soc. chim. France*, 1986 (1960).