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Metal Cluster Structural Data from Vibrational Frequencies in Os_3 Systems of C_{2v} Symmetry

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The plastic metal cluster model enables a good optimized fit between calculated and observed ν(M–M) frequencies for C_{2v} Os_3 systems. Further, the stretching force constants of unbridged Os–Os bonds correlate with the crystallographic bond lengths. Alternatively, the frequency data may be used to obtain the Os–Os–Os bond angles in the cluster. The angles obtained are a sensitive function of the frequencies, but encouraging results are obtained.

Introduction

In a previous communication[1] we have demonstrated that the model for the vibrational spectra of metal clusters introduced by Quicksall and Spiro[2] gives rather good agreement with the ν(M–M) spectra of $Os_2Ru(CO)_{12}$ and $OsRu_2(CO)_{12}$ using data derived from $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$. This finding prompts the question of whether the model can be usefully extended to triangular metal clusters of yet lower symmetry.

The present contribution represents a first step in this extension by considering species which, although of the same actual symmetry as $M_2M'(CO)_{12}$, must be regarded as having a lower effective geometrical and electronic symmetry.

In the Quicksall and Spiro model only geometric coupling between the vibration of the metal atoms in a triangular cluster is included. The **G** matrix elements are angle dependent, and so it is reasonable that small distortions from a symmetric arrangement should be covered by the model. The bond stretching **F** matrix contains only diagonal terms, implying that the energy required to stretch one metal–metal bond is insensitive to whether adjacent metal–metal bonds are compressed or elongated.

More recently it has been demonstrated that the inclusion of an interaction constant in the **F** matrix does not improve agreement between Quicksall and Spiro's model and the experimental data.[3] In the present paper we extend the simple model to species containing triangles of metal atoms which are near or actually isosceles. The compounds on which we report in this study have had either their own structures determined or those of closely related species. We have studied $(\mu\text{-H})_2Os_3(CO)_{10}$,[4,5] $(\mu\text{-OC}_2H_5)_2Os_3(CO)_{10}$—the structure of the $\mu\text{-OCH}_3$ compound is known[6]—$(\mu\text{-H})(\mu\text{-HCCH}_2)Os(CO)_{10}$[7] and $(\mu\text{-H})(\mu\text{-SCH}_3)Os_3(CO)_{10}$—the structure of the $\mu\text{-SC}_2H_5$ species has been determined.[6] These all contain a triangular Os_3 unit which becomes progressively closer to equilateral along the series. However, the presence of bridging groups may mean that the electronic asymmetry differs from the geometric.

For the idealized C_{2v} arrangement of three metal atoms shown in Figure 1, the metal–metal stretching vibrations subtend the symmetry species 2 A_1 + B_1. A diagonal **F** matrix and complete **G** matrix give the frequency of the B_1 mode as proportional to

$$[\mu f_B(2 - \cos \vartheta_A)]^{1/2} \qquad (1)$$

where the notation of Figure 1 has been used. That is, assignment of the B_1 mode, together with a knowledge of the molecular geometry, gives a unique value of f_B. The two A_1 frequencies are proportional to

$$\left[\frac{\mu f_B}{2}(\cos \vartheta_A + 2) + \mu f_A \pm \frac{\mu}{2}\{[f_B(\cos \vartheta_A + 2) + 2f_A]^2 - 12 f_A f_B(\cos \vartheta_A + 1)\}^{1/2}\right]^{1/2} \qquad (2)$$

Expression 2 is less formidable than it appears because, with a knowledge of the molecular geometry and f_B from (1), f_A is the only unknown it contains. One need only consider either the plus or minus sign within expression 2 together with an experimental frequency to obtain f_A; the prediction of the third frequency than provides a check on the accuracy of the model. While this sequence has its attractions, we have been more concerned with that choice of f_A which gives the best fit to the experimental data and for this it is more convenient to express (2) as eq 3 where (+) and (−) represent expression

$$\frac{\nu_1(A_1)}{\nu_2(A_1)} = \frac{(+)}{(-)} \qquad (3)$$

2 taken with the indicated choice of sign. The calculation is readily iterated; small changes may be made to f_B, leading to consequential changes in f_A, until the best overall fit of the data to the theory is obtained. This sequence is equivalent to a least-squares fitting procedure.

The above analysis requires an unambiguous assignment of the three ν(M–M) spectral bands. The highest frequency mode will clearly be of A_1 symmetry because it correlates with the A_1' mode in D_{3h}. The lower frequency bands correlate with E′ in D_{3h} and, mutatis mutandis, we expect interaction between the two modes of A_1 symmetry in C_{2v} to lead to the order $A_1 > B_1 > A_1$. This is the sequence adopted in this work and which leads to consistent and good results.

Discussion

For a C_{2v} M_3 system, all ν(M–M) modes are both infrared and Raman active. However, in the "parent" D_{3h} system, the corresponding totally symmetric vibration is only Raman active and so it cannot be assumed that in C_{2v} all modes will be seen in both infrared and Raman spectra. In practice, although band coincidences are observed, it usually requires both infrared and Raman spectra to determine the three frequencies required for this work. Notwithstanding the fact that f_A may be rewritten in terms of force and interaction constants involving the bridging groups and that motion of these bridging groups may couple with the ν(M–M) modes, a rather good agreement may be obtained between the observed and calcu-

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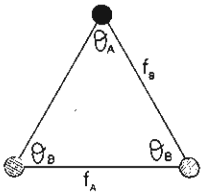

Figure 1. Schematic structure of the triangular Os_3 clusters and definition of force constants and angles.

Table I. Observed and Calculated Frequencies (cm^{-1}) of the M-M Stretching Modes

species	obsd	calcd
(μ-$OC_2H_5)_2Os_3(CO)_{10}$ (1)	170	170
	132	132
	104	104
(μ-H)(μ-$HCCH_2)Os_3(CO)_{10}$ (2)	168^a	169
	126^a	124
	116^a	115
(μ-H)(μ-$SCH_3)Os_3(CO)_{10}$ (3)	168	170
	130	127
	103	102
(μ-$H)_2Os_3(CO)_{10}$ (4)	187	188
	142	140
	97	97

[a] Data from ref 13.

Table II. Values of the Force Constants (mdyn/Å)

species	f_A	f_B
(μ-$OC_2H_5)_2Os_3(CO)_{10}$ (1)	0.75	1.22
(μ-H)(μ-$HCCH_2)Os_3(CO)_{10}$ (2)	0.95	1.12
(μ-H)(μ-$SCH_3)Os_3(CO)_{10}$ (3)	0.70	1.20
(μ-$H)_2Os_3(CO)_{10}$ (4)	0.60	1.50
$Os_3(CO)_{12}$ (5)	1.01	

lated frequencies (Table I). It is to be noted that all data, crystallographic and spectroscopic, refer to the solid state and that solid-state effects on metal–metal stretching frequencies are small. The force constants which result from the above iterated analysis are detailed in Table II. It is to be noted that the force constant f_A, which is associated with an Os–Os unit which is doubly bridged, is invariably smaller than f_B, which corresponds to an unbridged Os–Os bond in the same molecule. The qualitative reason for this difference in clear; in an Os–L–Os unit of C_{2v} symmetry there are three internal coordinates of A_1 symmetry (symmetrical ν(Os–L), symmetrical δ(Os–L–Os), and ν(Os–Os)) but only two A_1 normal coordinates. This redundancy means that the internal coordinates are not orthogonal and that there will be no normal coordinate which closely approximates to ν(Os–Os). This same conclusion is reached as a result of the recognition of G matrix effects: it is physically impossible to change the Os–Os bond length without simultaneously changing the Os–L–Os angle, the Os–L bond lengths, or both. Rather similar considerations apply to Os(μ-L)$_2$Os and Os(μ-L)(μ-L′)Os systems. We conclude that f_A values would not be expected to vary systematically in our systems; indeed it would probably not be meaningful to attempt to rationalize their values except in the context of a much more detailed vibrational analysis. However, the low values of f_A (particularly for the (μ-H)$_2$ species) may be held to provide indirect support for the "no Os–Os bond" model of such bridges.[5]

On the other hand f_B relates to the stretching of an unbridged Os–Os bond in all of the compounds. It would be reasonable to expect that f_B should be a function of the Os–Os bond length since such a relationship is commonly observed.[8]

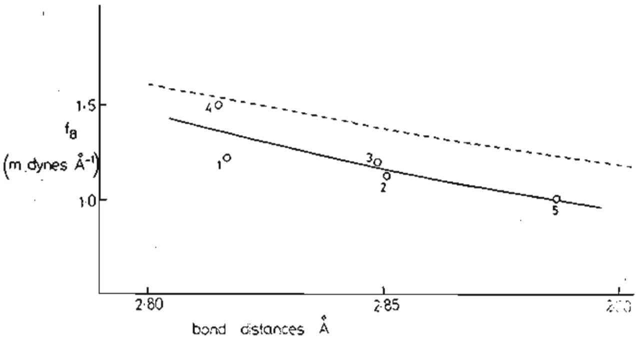

Figure 2. Comparison of the force constant f_B and the bond lengths. Species are indicated by the numbers used in Table II. The dashed line is that given by the Badger equation.[8a]

Table III. Comparison between the Crystallographically Determined Angles and Those Calculated from (4) (Deg)

	cryst		calcd	
	ϑ_A	ϑ_B(av)	ϑ_A	ϑ_B
(μ-$OC_2H_5)_2Os_3(CO)_{10}$ (1)	66.2^b	56.9^b	68.4	55.4
(μ-H)(μ-$HCCH_2)Os_3(CO)_{10}$ (2)	60.1	59.9	$60.1^{1\,a}$	59.9
			$66.8^{2\,a}$	56.6
(μ-H)(μ-$SCH_3)Os_3(CO)_{10}$ (3)	60.3^c	59.8^c	66.5	56.7
(μ-$H)_2Os_3(CO)_{10}$ (4)	56.9	61.5	60.3	59.8

[a] Values calculated setting the quantity under the square root in eq 4 positive (1) or equal to 0 (2). See text. [b] For the μ-OCH_3 compound. [c] For the μ-SC_2H_5 compound.

A plot which is different from, but related to, the Badger rule curve is obtained as is evident from Figure 2, where the two are compared. It seems that for isosceles systems approximate bond length data may be obtained from f_B values. The three spectral observations may be used to obtain f_A, f_B, and ϑ_A values from the equations given above. The equation which relates ϑ_A to the observed frequencies is eq 4 where $\nu_1 \equiv \nu_1(A_1)$, $\nu_2 \equiv \nu_2(A_1)$, and $\nu_3 \equiv \nu(B_1)$.

$$\cos \vartheta_A = \{8\nu_1^2\nu_2^2 + 3\nu_3^2(\nu_1^2 + \nu_2^2) - 9\nu_3^4 \pm 3\nu_3^2[(\nu_3^2 - 3(\nu_1^2 + \nu_2^2))^2 - 32\nu_1^2\nu_2^2]^{1/2}\}/[4\nu_1^2\nu_2^2 + 6\nu_3^2(\nu_1^2 + \nu_2^2) + 6\nu_3^4] \quad (4)$$

It should be noted that setting $\nu_2 \equiv \nu_3$ does not lead to an immediate solution of eq 4—accidental degeneracy between $\nu_2(A_1)$ and $\nu(B_1)$ can occur when $\vartheta_A \neq 60°$. However, setting $\nu_2 = \nu_3$ and $\cos \vartheta_A = {}^1/_2$ immediately leads to the relationship $\nu_1 = 2^{1/2}\nu_2$, a relationship first recognized by Quicksall and Spiro. Equation 4 has two solutions depending on the choice of signs on the right hand side. If calculated data (such as those of Table I) are substituted into the equation, then an accurate value of ϑ_A is obtained, which is not surpising because the experimental ϑ_A was part of the input into the calculated data. However, to obtain this agreement it was always necessary to select the plus sign in front of the square root in (4) and this is also the case for all of other calculations using (4).

A comparison between ϑ_A values obtained from (4) and the X-ray values is given in Table III. The calculated ϑ_A values are extremely sensitive to the input data. Roughly speaking, a change of 1 cm^{-1} in any one frequency leads to a change in bond angle of ca. 1°. However, as is clear from the form of (4), if all frequencies are changed by the same multiplicative factor no change in ϑ_A value results. Constant errors in all frequency data therefore lead to relatively small changes in ϑ_A. The sensitivity of calculated ϑ_A values is well illustrated by the compound (μ-H)(μ-$HCCH_2)Os_3(CO)_{10}$, where, for the experimental frequencies, no solution of (4) was obtained (because the quantity under the square root in (4) becomes small but negative). However, for the calculated data for the same compound (Table I), where the difference from the

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[8] (a) P. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935); (b) W. Gordy, *ibid.*, **14**, 305 (1946).

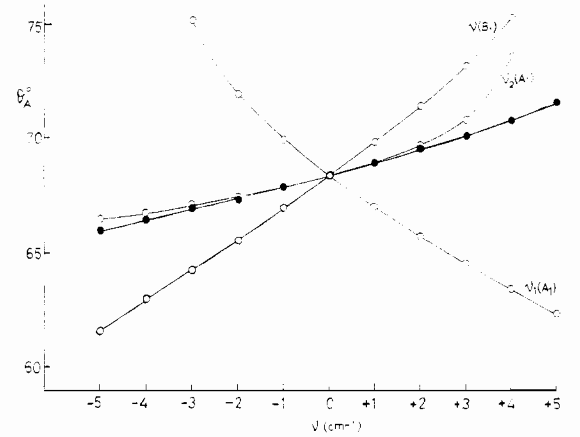

Figure 3. Variation of calculated value of ϑ_A with changes of input frequencies into eq 4 for $(\mu\text{-}OC_2H_5)_2Os_3(CO)_{10}$. At $\nu = 0$: $\nu_1(A_1) = 169$ cm^{-1}, $\nu_2(A_1) = 104$ cm^{-1}, and $\nu(B_1) = 132$ cm^{-1}. Open circles indicate the change of a single frequency; closed circles, the simultaneous change of all the frequencies.

experimental frequencies is a maximum of 2 cm^{-1}, an accurate value of ϑ_A was obtained. The sensitivity of the calculated ϑ_A values to changes of input frequencies for the compound $(\mu\text{-}OC_2H_5)_2Os_3(CO)_{10}$ is shown in Figure 3.

The experimental frequencies used in this paper were obtained before (4) was derived. In retrospect, it would have been possible to reinterpret the spectra to give frequencies differing by ca. 1 cm^{-1} from these presented in this paper but which gave even better "agreement" between experimental and calculated data in Table III. We did not feel it appropriate to do this but recognize that in future applications of (4) frequency accuracy will be essential, perhaps using curve fitting procedures to obtain peak frequencies with precision.

The data in Table III show an encouraging agreement between experimental and calculated values, particularly in view of our use of data which was not specifically frequency optimized. With such data, the sensitivity of (4) suggests that quite accurate values could result. Further, (4) offers the possibility that changes of angle can be determined as a function of state of matter or of other variables such as pressure and temperature.

Finally, recognizing that in those species containing two different types of bridging ligands the osmium triangles show minor deviations from isosceles, we have considered a more general triangle of osmium atoms in which each osmium–osmium edge of the triangle is associated with a different force constant. While variations in f_B and f_C from the f_B values given in Table II by up to ±ca. 0.03 mdyn Å^{-1} lead to marginal improvement in frequency fits, these improvement were not sufficient to affect the data in Table I. Since such calculations contain three unknown force constants, they do not offer the possibility of angle calculations.

Conclusions

This paper attempts to find answers to two questions. Firstly, does the "plastic metal atom cluster" model provide a self-consistent description of the ν(M–M) vibrational spectra of isosceles, or near-isosceles, triatomic metal clusters? As is evident from Table I, the agreement between experimental and calculated data, with the crystallographically determined bond angle, is good. Further, the f_B values obtained behave in a reasonable manner (Figure 2).

The second question is, "Can geometrical data be obtained from vibrational frequencies?" Here, again, the outcome is encouraging (Table III) although it will require frequencies obtained at the limits of precision to fully test the model. The frequency data also enable f_B to be determined uniquely. However, the correlation between f_B obtained in this manner and crystallographic bond lengths is markedly inferior to the correlation using optimized frequency fit values of the preceding paragraphs.

In general, then, the "plastic metal cluster" model provides a rather good basis for the discussion of ν(M–M) vibrations, at least in triangular clusters. Further, it offers the possibility that molecular geometries may be obtained in some detail from vibrational spectra. As with other systems to which the plastic metal cluster model has been applied, coupling with other molecular modes has been ignored. It seems to be a feature of the model that, with this neglect, it gives rather good fits to experimental data. The present work is no exception.

Finally, equations such as (4) here may be derived for other metal cluster systems. This aspect will be the subject of a future communication.

Experimental Section

The carbonyl compounds $(\mu\text{-}H)_2Os_3(CO)_{10}$,[9] $(\mu\text{-}OC_2H_5)_2Os_3(CO)_{10}$,[10] $(\mu\text{-}H)(\mu\text{-}HCCH_2)Os_3(CO)_{10}$,[11] $(\mu\text{-}H)(\mu\text{-}SCH_3)Os_3(CO)_{10}$[12] were prepared according to well-known procedures.[13]

Raman spectra were recorded for samples contained in a capillary tube at room temperature by a Spex 1401 double-beam monochromator and Spectra Physics 165 Ar/Kr laser using 6471- and 6764-Å exciting lines and a resolution of ca. 3 cm^{-1}.

Infrared spectra in the low-wavenumber region were recorded on an RIIC FT 720M interferometer at ca. 5-cm^{-1} resolution.

The dark brown $(\mu\text{-}H)_2Os_3(CO)_{10}$ gives a poor Raman scattering spectrum, and only two bands are clearly resolved at 187 and 142 cm^{-1}, the last one being coincident with a strong IR absorption. The third frequency appears as a medium-intensity infrared band at 97 cm^{-1}.

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