

$C_6H_6 \cdot AgClAl_4$ .<sup>21</sup> In the former, this asymmetry manifested itself in statistically disordered Ag positions, but it is unambiguous in the latter. It is not likely that molecular packing would be the cause of this asymmetry in metal-carbon distances, because the packing is quite different in  $C_3H_6 \cdot AgClO_4$ ,  $C_6H_6 \cdot CuAlCl_4$  and  $C_6H_6 \cdot AgAlCl_4$ . A similar asymmetry in Cu-C distances has been observed in a copper(I)-olefin complex.<sup>9f</sup>

We suggest that this asymmetry between the closest carbon-to-metal distances is a fundamental property of metal ion-aromatic complexes. Further, we suggest that the reason for this asymmetry is a compromise between the acceptor properties of the metal ion, or coordinated metal ion, and the donor properties of this same ion. That is, if the acceptor orbital were a 4s- or an  $sp^3$ -hybrid orbital, the most advantageous position would be at the point of greatest electron density of the ring, directly above one of the carbon atoms. On the other hand, using inner d orbitals for the metal ion as donor, the most likely position would be above and symmetrically between two carbon atoms of the aromatic system. Hence, a compromise between these

two effects is reached and unequal metal-carbon distances result. However, in platinum- and palladium-olefin complexes, there has been no evidence for different metal-to-carbon distances, but it is quite likely that details of the bonding may be quite different for olefin complexes.

Although the bond distances alternate in lengths around the ring and suggest a cyclohexatriene system, the errors are sufficiently large that this variation of bond distances may not be real and caution should be applied to any interpretations based on C-C distances in this complex.

It is, in fact, an interesting question as to why the complex forms at all. In the presence of chlorine donors it is surprising that the metal-aromatic bond is preferred to M-Cl interactions. The answer may be that in the packing of anhydrous  $CuAlCl_4$  large voids remain, and it becomes energetically favorable to form metal ion-aromatic bonds over metal ion-chlorine bonds. We plan to investigate the crystal structure of anhydrous  $CuAlCl_4$  in the near future.

**Acknowledgment.** We wish to acknowledge the financial support of NSF Grant GP-1575.

## Cage Compounds Containing the Trirhenium(III) Cluster: $Re_3Br_3(AsO_4)_2(DMSO)_3$ <sup>1</sup>

F. Albert Cotton and Stephen J. Lippard<sup>2</sup>

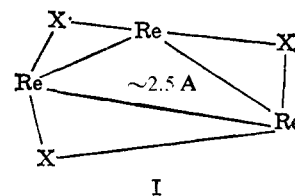
*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.*

*Received January 12, 1966*

**Abstract:** The preparation and molecular structure of  $Re_3Br_3(AsO_4)_2(DMSO)_3$ , a representative member of the new class of compounds  $Re_3X_3(MO_3 \text{ or } 4)_2L_n$ , are discussed. From the visible spectrum, it is apparent that the trirhenium(III) metal atom cluster occurs in this compound. Further insights into its structure are obtained from a detailed analysis of the infrared spectrum. Apparently, two tridentate arsenate ions have replaced the six axial halide ions in the  $Re_3Br_3$  molecule to form a cage which incorporates the cluster. The solvent (DMSO) molecules are thought to occupy nonbridging equatorial sites in the cluster.

The existence of the trirhenium(III) metal atom cluster in complexes prepared from rhenium(III) chloride and rhenium(III) bromide has been well established.<sup>3-11</sup> Studies by Robinson and Fergusson<sup>11</sup> have shown that, of the twelve halogen atoms (six

axial, three equatorial bridging, and three equatorial nonbridging) in the  $Re_3X_{12}^{3-}$  ion, only three, presumably the equatorial bridging ones, are not subject to exchange with thiocyanate or radioactively labeled halide ions. Apparently, then, the stable structural unit in the trirhenium(III) metal atom cluster compounds is the  $Re_3X_3$  group (I).



From the known geometry (*cf.* ref 3-8) and net charge (+6) of I, it seemed likely to us that anions such

- (1) Supported by the U. S. Atomic Energy Commission.
- (2) National Science Foundation Postdoctoral Fellow, 1965-1966.
- (3) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1106 (1963).
- (4) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).
- (5) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181, (1964).
- (6) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).
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- (8) F. A. Cotton and S. J. Lippard, *ibid.*, **4**, 59 (1965).
- (9) F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964).
- (10) F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).
- (11) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).

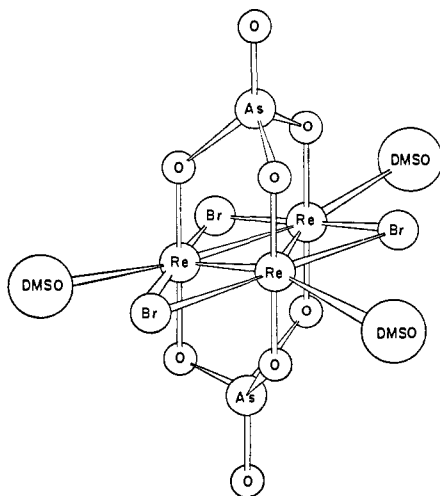


Figure 1. Perspective view of the proposed structure of the molecule  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ .

as  $\text{AsO}_4^{3-}$ , in which three oxygen atoms define an equilateral triangle of edge  $\sim 2.5$  Å, would be ideally suited for forming neutral adducts with I of the type  $\text{Re}_3\text{X}_3(\text{AsO}_4)_2$ . Thus we began an extensive investigation of the reaction of the rhenium(III) halides,  $\text{Re}_3\text{Cl}_3$  and  $\text{Re}_3\text{Br}_3$ , with the  $\text{MO}_3^{3-}$  or  $\text{MO}_4^{3-}$  anions, where  $\text{M} = \text{As}, \text{P}$ , etc. In this paper, we discuss the preparation and molecular structure of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  as a typical member of the series.

### Experimental Section

**Preparation of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ .** To the red solution formed by the addition of 1.0 g (0.8 mmole) of rhenium(III) bromide to 50 ml of acetone<sup>10</sup> was added 1.0 g ( $\sim 2$  mmoles) of silver arsenate. The heterogeneous mixture was vigorously agitated for 4 hr. Subsequent filtration yielded a solid product mixture and a clear filtrate. The solid was then extracted with 50 ml of dimethyl sulfoxide (DMSO) containing a few drops of 48% HBr for 15 min on the steam bath ( $\sim 90^\circ$ ). The resultant mixture was filtered to give a white solid (AgBr) and a deep red filtrate. To the latter was added ca. 300 ml of tetrahydrofuran. After cooling the solution to  $0^\circ$  and scratching the walls of the container with a glass rod, a flocculent red solid separated out and was collected by filtration. The yield, after drying at  $100^\circ$  *in vacuo* over  $\text{P}_2\text{O}_5$  for 24 hr., was 0.5 g ( $\sim 50\%$ ).

*Anal.* Calcd for  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{CH}_3)_2\text{SO}_3$ : Br, 18.3; C, 5.50; H, 1.38. Found: Br (average of two independent preparations), 18.5; C, 5.78; H, 1.47.

**Physical Measurements.** Infrared spectra were taken with both the Perkin-Elmer Model 337 and 521 spectrometers on samples mullied in Nujol or pressed into KBr pellets. Visible spectra were run in DMSO on the Cary 14 spectrophotometer using 1-cm matched quartz cells. A 114.6-mm Debye-Scherrer rotating-sample powder camera and  $\text{Cu K}\alpha$  radiation filtered through nickel were used in the attempt to get a powder pattern of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ .

**Computations.** Force constants used in the analysis of the infrared spectra were computed using a computer program<sup>12</sup> which adjusts the constants to give the best least-squares fit of the calculated frequencies to the measured ones. Details of the calculation are discussed below.

### Results and Discussion

**Preparations.** When solutions of rhenium(III) chloride or bromide in acetone are vigorously shaken with the silver salt of  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ , or  $\text{AsO}_3^{3-}$ , a product

(12) J. H. Schachtschneider and R. A. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

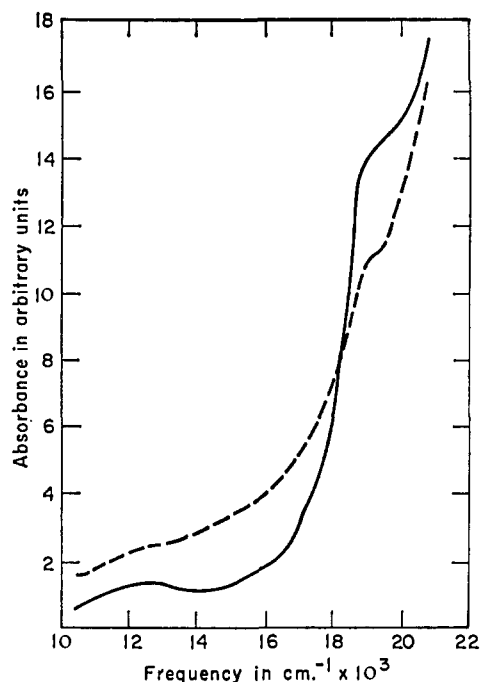


Figure 2. Visible spectra of compounds thought to contain the trirhenium(III) metal atom cluster dissolved in strong donor solvents: solid line,  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  in DMSO; dashed line,  $\text{Re}_3\text{Br}_3(\text{C}_6\text{H}_5\text{N})_3$  in pyridine.

mixture containing silver halide and the desired cage-cluster addition compound precipitates. The great insolubility of both products makes their separation quite difficult. Only by using strong donor solvents, such as DMSO, dimethylformamide (DMF), methanol, or pyridine, which presumably are capable of "solubilizing" the trirhenium(III) cluster by reacting to fill one or more of its nonbridging equatorial positions, can the separation be effected. The compound obtained by subsequent reprecipitation from the donor solvent medium by the addition of a second solvent (*e.g.*, tetrahydrofuran; *vide supra*), then, invariably contains bound solvent molecules.

The preparation of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  described in the Experimental Section of this paper, has been repeated several times in our laboratory, and this appears to be the only compound which consistently contains three bound solvent molecules. Work now in progress indicates that others, such as  $\text{Re}_3\text{Cl}_3(\text{AsO}_4)_2(\text{DMSO})_2$ ,  $\text{Re}_3\text{X}_3(\text{AsO}_3)_2(\text{DMSO})_2$ ,  $\text{Re}_3\text{Cl}_3(\text{AsO}_3)_2(\text{DMF})_2$ , and  $\text{Re}_3\text{Br}_3(\text{PO}_4)_2(\text{DMSO})_2$ , have also been obtained in similar reactions and will be reported later. At present, we intend to show that, as a representative example of the entire class of compounds  $\text{Re}_3\text{X}_3(\text{MO}_3 \text{ or } \text{MO}_4)_2\text{L}_n$ , the physical properties of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  are consistent with the structure shown in Figure 1.

**Physical Properties and Molecular Structure of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ .** X-Ray powder diffraction studies indicate that the  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  obtained as described above is amorphous. Although this is not surprising in view of the method of preparation, it does preclude for the present a direct single-crystal X-ray structural investigation. On the basis of infrared and visible spectral information, however, it appears that the structure is probably the one shown in Figure 1.

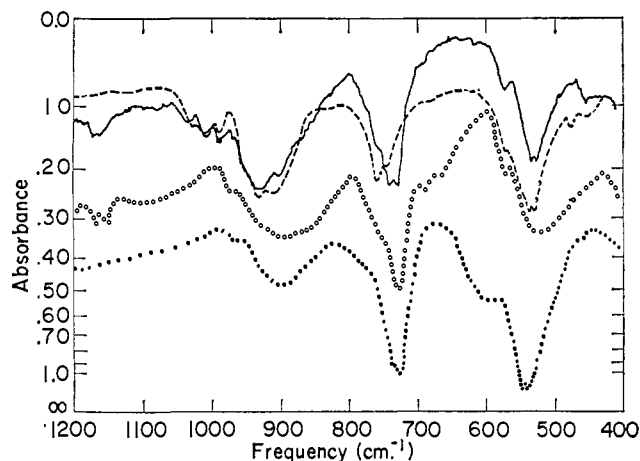
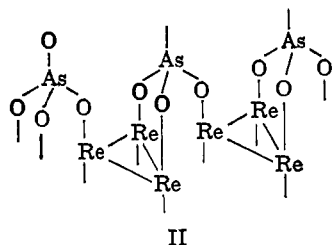


Figure 3. Infrared spectra of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  mull in Nujol (solid line) and pressed into a KBr disk (dashed line); and, of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2\text{L}_n$  mull in Nujol, where L = dimethylformamide (open circles) or methanol (closed circles).

Previous experiments in our laboratories<sup>9,10</sup> and elsewhere<sup>11</sup> have established that, in the visible spectrum, two bands at *ca.* 12–13,000 and 19–20,000  $\text{cm}^{-1}$ , having relative intensities of 1:3, may be found for all compounds known or thought to contain the  $\text{Re}_3\text{X}_3$  group dissolved in solvents such as chloroform, acetone, or acetonitrile. In more strongly donating solvents, such as dimethyl sulfoxide or pyridine, the low-energy band becomes considerably broadened.<sup>13</sup> The visible spectrum of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ ,  $1.5 \times 10^{-4} M$  in DMSO, appears in Figure 2. For comparison purposes, we have reproduced<sup>14</sup> the spectrum of  $\text{Re}_3\text{Br}_3(\text{C}_5\text{H}_5\text{N})_3$  in pyridine. From the similarity of these spectra, it seems likely that, in the adduct of rhenium(III) bromide and silver arsenate, the  $\text{Re}_3\text{Br}_3$  moiety of the initial  $\text{Re}_3\text{Br}_3$  remains intact.

Although the visible spectrum of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  is perfectly consistent with the structure proposed in Figure 1, other structures may be drawn which also contain the  $\text{Re}_3\text{Br}_3$  group. Thus, for example, a polymer such as that shown below (II), where the arsenate groups form bridges between neighboring trirhenium(III) clusters, might conceivably occur.



While a structure such as that shown in II seems unlikely on the basis of steric requirements, to lend further support to the structure proposed (Figure 1), we have undertaken a rather thorough infrared spectral analysis of the compound, the details of which follow.

The 400–1200- $\text{cm}^{-1}$  region of the infrared spectrum of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ , mull in Nujol, is shown in

(13) This broadening has been ascribed<sup>14</sup> previously to a time-averaged incomplete occupation of the coordination sphere of the rhenium atom cluster.

(14) S. J. Lippard, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1965.

Figure 3. The broad band at  $\sim 925 \text{ cm}^{-1}$  is partially due to the S=O stretching frequency of coordinated DMSO, as previously assigned in similar complexes of the rhenium(III) halides with sulfoxides.<sup>10</sup> When the  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2$  cluster was prepared using hot dimethylformamide (DMF) or methanol instead of DMSO to separate it from silver bromide (*vide supra*), however, compounds containing DMF or  $\text{CH}_3\text{OH}$  instead of DMSO in the nonbridging equatorial positions of the trirhenium(III) cluster were isolated. The 400–1200- $\text{cm}^{-1}$  regions of the infrared spectra of these adducts also appear in Figure 3, from which it is clear that a broad band, centered at approximately 900  $\text{cm}^{-1}$ , is characteristic of the  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2$  group. It can also be seen from the figure that strong bands occur at 740, 725, 550, and 539  $\text{cm}^{-1}$  as well as a weaker band at 572  $\text{cm}^{-1}$  (shoulder). These bands are, in all probability, not due to coordinated solvent, for, as evident from Figure 3, they occur at the same frequency for L = DMSO, DMF, and methanol. As further evidence for this point, the infrared spectrum of a Nujol mull of the crude reaction product of  $\text{Re}_3\text{Br}_3$  and  $\text{Ag}_3\text{AsO}_4$  was taken before the addition (*vide supra*) of a donor solvent. Strong bands in the 700–725 and 540–550- $\text{cm}^{-1}$  regions were observed. That the band at 725  $\text{cm}^{-1}$  does not result entirely from Nujol was verified by running the spectrum of a sample of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  pressed into a KBr disk (Figure 3).

Now, let us presume that the structure of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  is as shown in Figure 1. It is then a reasonable assumption that only the As–O and Re–O stretches of the  $(\text{OAsO}_3)_2\text{Re}_3$  fragment will contribute to the infrared spectrum in the region above 400  $\text{cm}^{-1}$ . If, in addition, there is no coupling from one-half of the molecule to the other, then, under  $C_{3v}$  symmetry, there are seven As–O or Re–O oscillators. Using this model, and neglecting Re–O to Re–O and Re–O to As=O interactions, a secular equation was constructed and factored by symmetry (Table I).<sup>15</sup>

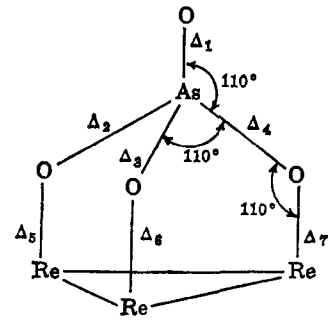
As a first approximation, values of 6.0 mdyne/A for the As=O and 4.0 mdyne/A for the As–O and Re–O force constants, and 0.5 mdyne/A for the As=O to As–O, As–O to As–O, and As–O to Re–O interaction constants were assigned. The secular equation was then solved and the infrared spectrum assigned as follows:  $\nu^{\text{A}}_{\text{As}=\text{O}} = 900 \text{ cm}^{-1}$ ;  $\nu^{\text{A}}_{\text{As}-\text{O}} = 740 \text{ cm}^{-1}$ ;  $\nu^{\text{E}}_{\text{As}-\text{O}} = 725 \text{ cm}^{-1}$ ;  $\nu^{\text{A}}_{\text{Re}-\text{O}} = 539 \text{ cm}^{-1}$ ;  $\nu^{\text{E}}_{\text{Re}-\text{O}} = 550 \text{ cm}^{-1}$ . Finally, with these assignments, the three diagonal force constants were adjusted by the least-squares method to give the best fit to the observed frequencies, while the off-diagonal (interaction) constants were fixed at 0.5 mdyne/A.<sup>16</sup> The final values of the force constants together with a list of observed and calculated frequencies, calculated after the last cycle of least-squares refinement, may be found in Table II.<sup>16a</sup>

(15) See, for example, E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(16) To test the validity of this procedure, we subsequently held the refined diagonal force constants fixed and varied the off-diagonal ones. They did not vary by more than  $\pm 0.13$  mdyne/A from the assumed value of 0.5 mdyne/A (*cf.* Table II).

(16a) NOTE ADDED IN PROOF. Since the submission of this article, a paper has appeared in the literature (A. Merijanjan and R. Zingaro, *Inorg. Chem.*, **5**, 187 (1966)) in which a value of 6.9 mdyne/A is given for the force constant of the "As–O" bond in several trialkylarsine oxides. This compares reasonably well with our result (6.34 mdyne/A) for the As=O bond in  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ .

**Table I.** Information Pertaining to Calculation of MO Stretching Modes (M = Re, As) in  $\text{OAsO}_3\text{Re}_3$  "Half-Molecule" Group of  $C_{3v}$  Symmetry. Assumed Molecular Geometry and Definition of Internal Coordinates and Force Constants

Symmetry species <sup>a</sup>	Symmetry coordinates	Force constants		Factored secular equations <sup>b</sup>		
		Constant	Interaction	$ F   G  -  E  \lambda = 0$		
				$F_a$ $\Delta_1 \cdot \Delta_1$ $F_b$ $\Delta_2 \cdot \Delta_2, \Delta_3 \cdot \Delta_3, \Delta_4 \cdot \Delta_4$ $F_c$ $\Delta_5 \cdot \Delta_5, \Delta_6 \cdot \Delta_6, \Delta_7 \cdot \Delta_7$ $F_{ab}$ $\Delta_1 \cdot \Delta_2, \Delta_1 \cdot \Delta_3, \Delta_1 \cdot \Delta_4$ $F_{bb}$ $\Delta_2 \cdot \Delta_3, \Delta_3 \cdot \Delta_4, \Delta_4 \cdot \Delta_2$ $F_{bc}$ $\Delta_2 \cdot \Delta_5, \Delta_3 \cdot \Delta_6, \Delta_4 \cdot \Delta_7$ All other possible interactions were taken as zero		
$A_1(\text{R, IR})$	$S_{\text{As-O}} = \Delta_1$ $S_{\text{As-O}} = \frac{1}{\sqrt{3}}(\Delta_2 + \Delta_3 + \Delta_4)$ $S_{\text{Re-O}} = \frac{1}{\sqrt{3}}(\Delta_5 + \Delta_6 + \Delta_7)$	$F_a$ $\frac{3}{\sqrt{3}}(F_{ab})$ $\frac{3}{\sqrt{3}}(F_{ab})$ $(F_b - 2F_{bb})$ 0 $F_{bc}$ $F_c$	$(\mu_{\text{As}} + \mu_0)$ $\frac{3}{\sqrt{3}}(\mu_{\text{As}} \cos 110^\circ)$ 0	$\frac{3}{\sqrt{3}}(\mu_{\text{As}} \cos 110^\circ)$ $(\mu_{\text{As}} + \mu_0 + 2\mu_{\text{As}} \cos 110^\circ)$ $(\mu_0 \cos 110^\circ)$	0 $(\mu_0 \cos 110^\circ)$ $(\mu_{\text{Re}} + \mu_0)$	
$E(\text{R, IR})$	$S_{\text{As-O}} = \frac{1}{\sqrt{6}}(2\Delta_2 - \Delta_3 - \Delta_4)$ $S_{\text{As-O}} = \frac{1}{\sqrt{2}}(\Delta_3 - \Delta_4)$ $S_{\text{Re-O}} = \frac{1}{\sqrt{6}}(2\Delta_5 - \Delta_6 - \Delta_7)$ $S_{\text{Re-O}} = \frac{1}{\sqrt{2}}(\Delta_6 - \Delta_7)$	$(F_b - F_{bb})$ $F_{bc}$ $F_{bc}$ $F_c$	$(\mu_0 + \mu_{\text{As}} - \mu_{\text{As}} \cos 110^\circ)$ $\mu_0 \cos 110^\circ$	$\mu_0 \cos 110^\circ$ $\mu_{\text{Re}} + \mu_0$		

<sup>a</sup> R = Raman active; IR = infrared active. <sup>b</sup>  $|E|$  = unitarity matrix;  $\mu$  = reciprocal mass;  $\lambda = 5.889 \times 10^{-2}(\nu^2)$ , where  $\nu$  is the frequency in  $\text{cm}^{-1}$ ; see ref 15.

**Table II.** Observed and Calculated Frequencies for the Infrared Spectrum (400–1200- $\text{cm}^{-1}$  region) of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  Mullied in Nujol<sup>a</sup>

Obsd, $\text{cm}^{-1}$	Calcd, <sup>b</sup> $\text{cm}^{-1}$	Assignment
900 (strong, broad)	899	As=O; $A_1$
740 (strong)	760	As-O; $A_1$
725 (strong)	708	As-O; E
572 (weak, sh)	...	?
550 (strong)	547	Re-O; E
539 (strong)	540	Re-O; $A_1$

<sup>a</sup> The S=O stretching frequency at  $\sim 925 \text{ cm}^{-1}$  is not included.  
<sup>b</sup> Calculated as discussed in the text using values of 6.34, 4.19, and 2.89 mdyne/A for  $F_a$ ,  $F_b$ , and  $F_c$ , respectively, and 0.5 mdyne/A for all off-diagonal (interaction) force constants. By varying the interaction constants (see footnote 16), a better fit of the  $A_1$  and E As-O frequencies could be obtained, the calculated values being 742 and 724  $\text{cm}^{-1}$ , respectively. The final interaction constants were then 0.57, 0.37, and 0.47 mdyne/A for  $F_{ab}$ ,  $F_{bb}$ , and  $F_{bc}$ , respectively (see Table I).

From Table II, it is apparent that the five major bands in the infrared spectrum of  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  (Figure 2), exclusive of the S=O stretching frequency, may be accounted for using a simple model

derived from the structure proposed in Figure 1. Only the weak band (shoulder) at 572  $\text{cm}^{-1}$  cannot be assigned and, possibly, this may be the overtone of a band at much lower energies. Furthermore, it now seems rather unlikely that the compound has a structure such as II above, in which the low symmetry would be expected to result in a much more complicated spectrum in the 400–1200- $\text{cm}^{-1}$  region.

In summary, then, while direct X-ray structural confirmation is, at present, unattainable, spectral studies strongly suggest that  $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$  (and, by inference, probably all complexes in the class  $\text{Re}_3\text{X}_3(\text{MO}_3 \text{ or } 4)\text{L}_n$ ) has the structure shown in Figure 1. The visible spectrum verifies that the trirhenium(III) metal atom cluster is still intact and the infrared spectrum is consistent with, though it does not positively prove, the existence of a high degree of molecular symmetry ( $C_{3v}$ ) for the  $\text{OAsO}_3\text{Re}_3$  fragment. Further investigations of other compounds of this class are in progress and will be reported in due course.

**Acknowledgment.** We are grateful to the MIT Computation Center for access to the IBM 7094 computer.