Vibrational Spectra of Matrix-isolated Rhenium Trifluoride Dioxide and Rhenium Fluoride Trioxide: the Molecular Shape of ReF_3O_2[†]

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The vibrational spectrum of monomeric ReF_3O_2 isolated in inert-gas matrices has been studied using i.r. and Raman techniques. From a total of six possible structural models based on trigonal-bipyramidal or square-pyramidal geometries, only one structure [a trigonal bipyramid with equatorial oxygen atoms (C_{2v} symmetry)] satisfies the observed spectra in terms of selection rules and relative band intensities. A new synthesis of ReF_3O_2 has been utilised in the preparation of isotopically enriched ^{18}O material, the spectra of which confirm that ReF_3O_2 contains two equivalent oxygen atoms. This C_{2v} structure is thus analogous to that proposed for ClF_3O_2. The vibrational spectrum of $ReFO_3$ produced as a by-product during these studies is also discussed in detail.

THERE are frequently considerable differences between the structures and properties of transition-metal d^0 species and their non-transition-metal d^{10} analogues. Tungsten tetrafluoride oxide forms fluorine-bridged tetramers in the solid state, and readily dissociates to give square-pyramidal (C_{4v}) monomers,[1] but TeF_4O forms strongly *oxygen-bridged* dimers, and is unknown as a monomer.[2,3] In contrast, both OsF_2O_3 [4] and XeF_2O_3 [5] form trigonal-bipyramidal (D_{3h}) monomers. Iodine trifluoride dioxide resembles TeF_4O in forming strong oxygen-bridged dimers,[3] which dissociate into monomer species only at low pressures and elevated temperatures.[6] It is therefore clearly of interest to examine ReF_3O_2 and to compare, in particular, its structure with that of the isoelectronic compounds WF_4O and OsF_2O_3. Other related rhenium

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† No reprints available.

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[4] I. R. Beattie, H. E. Blayden, R. A. Crocombe, P. J. Jones, and J. S. Ogden, *J. Raman Spectroscopy*, 1976, **4**, 313.

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[6] W. E. Falconer and M. J. Vasile, personal communication.

compounds are the recently synthesised [7] ReO_2Me_3 which has been assigned to point group C_s, and $ReCl_3O_2$ for which only preparative details are available.[8] (An earlier report [9] of this compound is apparently in error.[10])

Rhenium trifluoride dioxide was originally prepared by the action of fluorine on ReO_2 or $K[ReO_4]$ in a flow system,[11] and more recently a static synthesis has also been described.[12] The vapour pressure of the liquid, the melting point, and boiling point have been determined,[13] but no structural parameters are available, although molecular-beam mass-spectrometric–electric-deflection studies have indicated [12] that the vapour above ReF_3O_2 contains monomers, which are polar, and also dimer species $Re_2F_6O_4$ which are apparently non-polar.

In this paper we report i.r. and Raman studies on matrix-isolated ReF_3O_2 together with a new preparative route to this compound which allowed us to carry out an i.r. matrix study of the ^{18}O-enriched material. Similar data are reported for $ReFO_3$ which was produced during this study as a result of the reaction between ReF_3O_2 and borosilicate glass. The ^{18}O experiments yield spectra which may readily be interpreted using either a simple two-parameter force field (for the Re–O stretching region) or in terms of a more complete vibrational analysis, on the basis of which it is possible to deduce the most probable structure of ReF_3O_2.

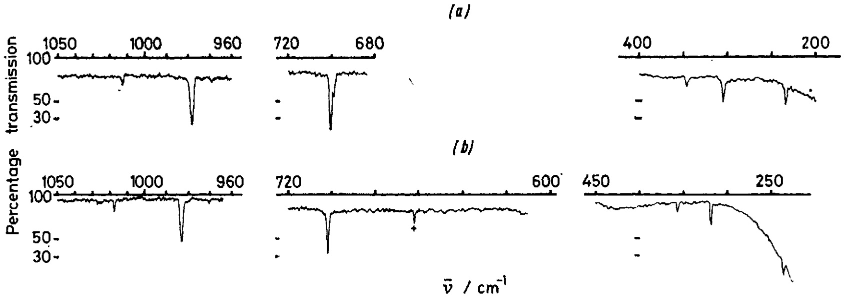

FIGURE 1 Infrared spectra of matrix-isolated $ReFO_3$: (a) argon matrix; (b) nitrogen matrix. (+), Band due to matrix-isolated CO

EXPERIMENTAL

The existing syntheses for ReF_3O_2 are not suitable for the preparation of small amounts of ^{18}O-enriched material and a more convenient synthesis was therefore devised based on previous experience with transition-metal fluoride oxide systems.[14] It has previously been shown [4,14] that when a 2 : 1 (mol ratio) mixture of OsO_4 and KBr is treated with an excess of BrF_3 an intermediate product is formed which on heating gives high yields of OsF_2O_3. This reaction is believed to proceed *via* the synthesis of an $[OsF_3O_3]^-$ salt, and as the corresponding $[ReF_4O_2]^-$ ion is known [15] the treatment of a 1 : 1 mixture of Re_2O_7 and KBr with an excess of BrF_3 was accordingly examined. This reaction produced a yellow solid which was not isolated but which liberated ReF_3O_2 and BrF_3 on heating *in vacuo*, suggesting that the intermediate may perhaps contain $[BrF_2]^+[ReF_4O_2]^-$ by analogy with the thermal decomposition of $[BrF_2]^+[TaF_6]^-$ into BrF_3 and TaF_5.[16]

In a typical synthesis, Re_2O_7 was initially prepared from elemental rhenium (0.106 g; B.D.H., 99.9%) by standard procedures [17] and an excess (*ca.* 3 cm^3) of BrF_3 (B.D.H., distilled before use) was then condensed on to a cold 1 : 1 mixture of KBr (*ca.* 0.034 g) and Re_2O_7. The BrF_3 was allowed to melt, whereupon a vigorous reaction ensued. After a few minutes, the BrF_3 was pumped off together with the bromine and oxygen produced. A pale yellow intermediate remained, which was then heated to 120—140 °C under dynamic vacuum. Flakes of ReF_3O_2 condensed on the cooler parts of the apparatus and were readily sublimed into break-seal ampoules. The overall yield, based on the initial weight of rhenium, was *ca.* 20%, and the Raman spectrum of the solid product had bands at 1 026vvs, 1 002s, 679m, 410m, 327m, 320m, 300w, 280w, and 115m cm^{-1}. Fluorine analysis [4] yielded $19.9 \pm 0.4\%$ (calc. for ReF_3O_2 : 20.6%). The somewhat lower experimental value is consistent with the presence of *ca.* 5% $ReFO_3$ as impurity. Subsequent manipulations were carried out in borosilicate apparatus equipped with greaseless taps, but despite extensive flaming small amounts of $ReFO_3$ were invariably produced whenever ReF_3O_2 was sublimed.

Samples of isotopically enriched ReF_3O_2 were prepared from ^{18}O-labelled Re_2O_7, which in turn was prepared by induction heating of a platinum boat containing rhenium powder to *ca.* 600 °C in an atmosphere of $^{16}O_2$–$^{18}O_2$. In this oxidation, uptake of oxygen ceased when the oxygen pressure fell below *ca.* 40 Torr.* The synthesis was then completed as above.

Matrix-isolation experiments were performed using Air Products CS202 Displex units in conjunction with Perkin-Elmer 225, 580, Beckman IR11, and Cary 82 spectrometers, and ancillary apparatus similar to that already described.[4] Slow spray-on rates for ReF_3O_2 were achieved by warming the sample to *ca.* 50 °C. Argon and nitrogen (Air Products, 99.999%) were used as matrix gases, and satisfactory spectra could be obtained after depositing the compound for *ca.*

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* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 dyn = 10^{-5} N.

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[8] I. A. Glukhov, N. A. El'manova, S. S. Eliseev, and M. T. Temurova, *Zhur. neorg. Khim.*, 1974, **19**, 309 (*Russ. J. Inorg. Chem.*, 1974, **19**, 168).

[9] H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J. Chem. Soc.*, 1932, 1104.

[10] J. H. Canterford and R. Colton, ' Halides of the Second and Third Row Transition Metals,' Wiley, London, 1968, p. 278.

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[14] M. A. Hepworth and P. L. Robinson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 24.

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30 min. In order to confirm the identity of the small amounts of $ReFO_3$ produced during these depositions, a series of matrix experiments was carried out on $ReFO_3$ prepared independently according to the method of Aynsley and Hair.[18] The compound $ReFO_3$ is more volatile than ReF_3O_2, and suitable deposition rates for this material were obtained by cooling the sample to *ca.* 5 °C. Raman spectra were excited using 5 145-Å radiation (Spectra Physics 170) with power levels at the sample in the range 100—500 mW.

RESULTS AND DISCUSSION

Initial i.r. experiments on ReF_3O_2 showed that all the stored samples contained small amounts of $ReFO_3$, SiF_4, and BF_3 produced by reaction with borosilicate glass at room temperature, and this behaviour is similar to that previously noted for OsF_2O_3.[4] These impurities could be completely removed by prolonged pumping at 0 °C, but in subsequent depositions our ReF_3O_2 spectra nevertheless showed some $ReFO_3$ contamination and it is therefore convenient to first discuss our supporting experiments on matrix-isolated $ReFO_3$.

TABLE 1

Vibrational data for some MXO_3 molecules

(*a*) Observed bands (cm^{-1})

		$ReFO_3$			$ReClO_3$			
$MnFO_3$ [a] I.r., gas	$TcFO_3$ [b] I.r., gas	I.r., matrix [c] (Ar)	I.r., matrix [c] (N_2)	Raman,[d] HF solution	I.r. and Raman,[e] matrix (Ar)	I.r. and Raman, liquid [f]	$ReBrO_3$ [g] I.r., solution	Mode
720.7	696	701	701	666	436, 427 [h]	435	195	ν_1 a_1
905.2	962	1 013.2	1 017.5	1 009	994	1 001	997	ν_2 a_1
337.7	317	305.5	318.5	321	291	303	332	ν_3 a_1
952.5	940	978.3	983	980	963	961	963	ν_4 e
373.7	347	346.9	354	403	337	344	350	ν_5 e
264.3	231	234.2	237	196	192	196	168	ν_6 e

(*b*) Calculated force constants

	$MnFO_3$ [a]	$TcFO_3$	$ReFO_3$ [i]	
F_R	6.40	7.371	8.507	mdyn $Å^{-1}$
F_{RR}	0.32	0.403	0.432	
F_r	4.52	4.577	5.027	
F_θ	0.98	1.189	1.269	mdyn Å rad^{-2}
$F_{\theta\theta}$	−0.03	0.095	0.075	
F_ϕ	0.65	0.589	0.702	

[a] Ref. 24. [b] Ref. 21. [c] This work. [d] Refs. 20 and 21. [e] Ref. 25. [f] Refs. 21—23. [g] Refs. 21 and 23. [h] $^{35}Cl-^{37}Cl$ isotopic splitting. [i] This work, based on argon-matrix frequencies.

Rhenium Fluoride Trioxide, $ReFO_3$.—This compound has C_{3v} symmetry,[19] and the six fundamentals ($\Gamma_{vib} = 3a_1 + 3e$) are i.r. and Raman active. No gas-phase or matrix-isolation studies have been reported for this compound, but six bands have been found in HF solution.[20] Figure 1 shows i.r. spectra obtained for $ReFO_3$ in argon and nitrogen matrices, and the frequencies observed are listed in Table 1 and compared with those observed for similar molecules. The scheme for numbering the fundamentals is that adopted by Selig and El-Gad.[20]

The bands at 1 013.2 and 978.3 cm^{-1} (argon matrix) clearly arise from the symmetric (ν_2, a_1) and antisymmetric (ν_4, e) Re–O stretching modes, and the band at 701 cm^{-1} is the unique Re–F stretch (ν_1, a_1). The assignment of the lowest-frequency band at 234.2 cm^{-1} to $\nu_6(e)$ is in keeping with existing data on molecules of this type, but there is considerable confusion in the literature over the assignment of the two remaining bending modes (ν_3 and ν_5) for these MXO_3 species. The latest assignments by Binenboym *et al.*[21] place $\nu_5 > \nu_3$ for $TcFO_3$ on the basis of i.r. band contours, and in accord with this these workers revise an earlier assignment [20] for $ReFO_3$ and similarly place ν_5 above ν_3. They further suggest that previous assignments for $TcClO_3$,[22] $ReClO_3$,[22,23] and $ReBrO_3$ [23] are in error. Reisfeld *et al.*[24] placed ν_5 higher than ν_3 in $MnFO_3$ but quoted values of *P–R* separations which would appear to allow the alternative assignment. The most recent and comprehensive study on $ReClO_3$ by Van Schalkwyk [25] presents convincing evidence that ν_5 is definitely above ν_3 and his results are quoted in Table 1. The choice for $ReFO_3$ remains open in the absence of vapour-phase depolarisation data, but in keeping with the conclusions of Van Schalkwyk,[25] Binenboym *et al.*,[21] and Reisfeld *et al.*[24] we assign the band at 305.5 cm^{-1} to $\nu_3(a_1)$ and that at 346.9 cm^{-1} to $\nu_5(e)$.

Table 1 shows that several of the $ReFO_3$ frequencies observed in these matrix studies are significantly different from those observed in HF solution,[20] and it is important to establish which set of frequencies is more appropriate to molecular $ReFO_3$. In the absence of strong dipolar effects, it is generally accepted that vibrational frequencies observed in matrices are frequently close to those observed in the gas phase, and it seems likely that for this system the use of HF as a solvent may introduce strong solute–solvent perturbations which might account,

[18] E. E. Aynsley and M. L. Hair, *J. Chem. Soc.*, 1958, 3747.

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[21] J. Binenboym, U. El-Gad, and H. Selig, *Inorg. Chem.*, 1974, **13**, 319.

[22] A. Guest, H. E. Howard-Lock, and C. J. L. Lock, *J. Mol. Spectroscopy*, 1972, **43**, 273.

[23] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 1960, **16**, 1148.

[24] M. J. Reisfeld, L. B. Asprey, and N. A. Matwiyoff, *Spectrochim. Acta*, 1971, **A27**, 765.

[25] G. J. Van Schalkwyk, Ph.D. Thesis, Southampton University, 1975.

in particular, for the abnormally low value for ν_6 observed by Selig.[20]

Vibrational analysis. The argon-matrix frequencies observed in this study were used to compute force constants for $ReFO_3$ with the aid of the SOTONVIB program.[26] A force field identical to that previously employed [24] for $MnFO_3$ was found to be satisfactory. This employs six potential constants: F_R, the principal Re–O stretch; F_r, the Re–F stretch; F_{RR}, the Re–O, Re–O interaction constant; F_θ, the O–Re–O bending constant; F_ϕ, the O–Re–F bending constant; and $F_{\theta\theta}$ the O–Re–O angle interaction constant. Structural parameters were take from the microwave study:[19] Re–O 1.692, Re–F 1.859 Å, O–Re–O 109.5°. The six force constants were adjusted so that they reproduced exactly the six observed frequencies for $ReF^{16}O_3$, and the values obtained are shown in Table 1. This Table also shows, for comparative purposes, the corresponding parameters in $MnFO_3$ and $TcFO_3$ using the same force field.

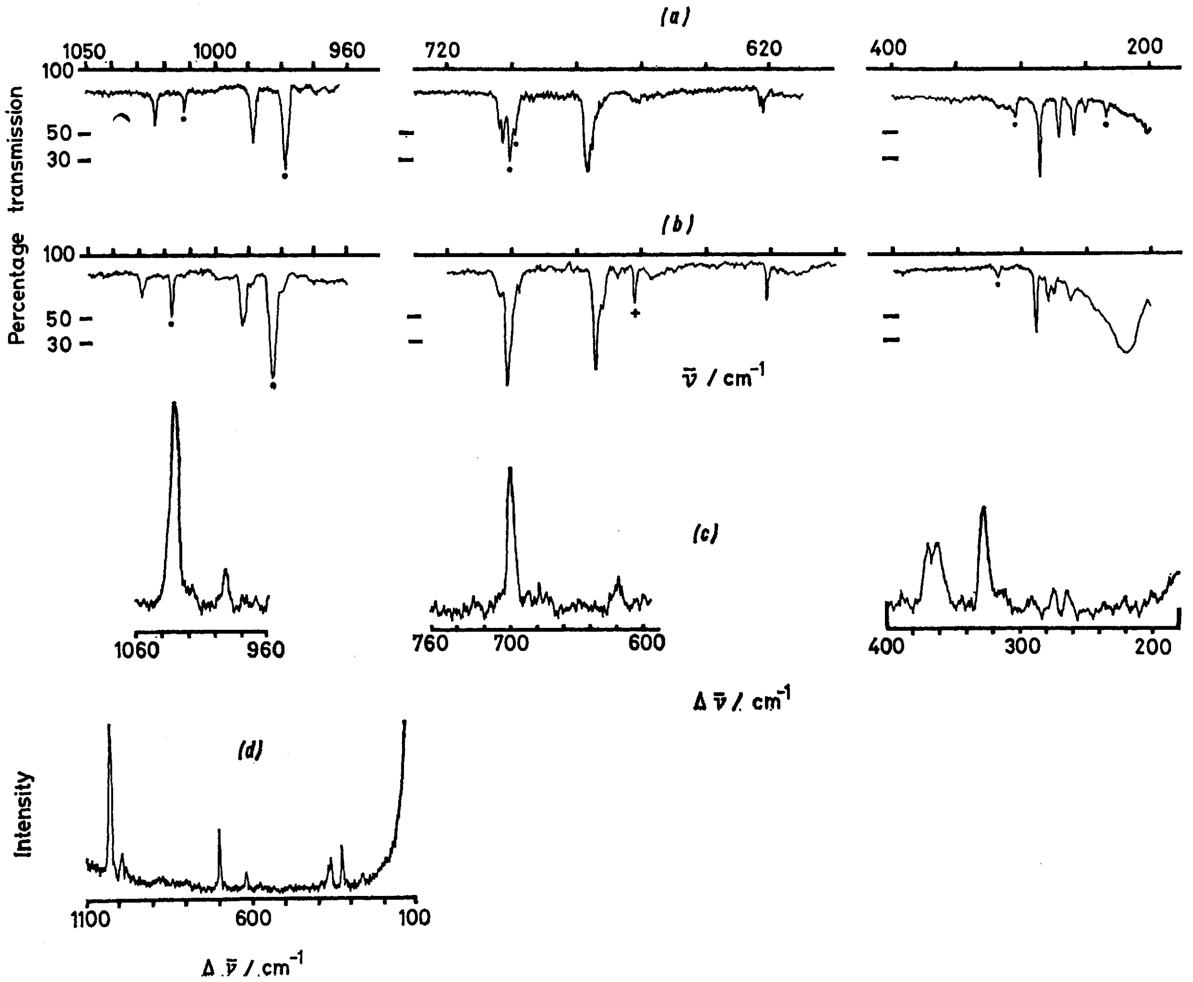

FIGURE 2 Infrared and Raman spectra of matrix-isolated ReF_3O_2: (*a*) i.r., argon matrix; (*b*) i.r., nitrogen matrix; (*c*) and (*d*) Raman, nitrogen matrix. (+), Band due to matrix-isolated CO_2; (*), bands due to matrix-isolated $ReFO_3$

Rhenium Trifluoride Dioxide, ReF_3O_2.—Figure 2(*a*) and (*b*) shows i.r. spectra of ReF_3O_2 isolated in argon and nitrogen matrices respectively, whilst Figure 2(*c*) and (*d*) shows Raman spectra of ReF_3O_2 in a nitrogen matrix. The i.r. spectra in particular show additional features due to $ReFO_3$. but, after accounting for these, these figures reveal nine i.r. and 11 Raman bands with eight observed coincidences, and this information is summarised in Table 2.

Before discussing detailed band assignments it is convenient to consider six possible structures for ReF_3O_2, three each being derived from trigonal-bipyramidal and square-pyramidal frameworks (Figure 3). Of these, structures (2) and (6), and (3) and (4) differ only in the sizes of interbond angles, and small angle deformations which retain full molecular symmetry are sufficient to render these identical. The numbers and activities of vibrational fundamentals for each of these models are also shown in this Figure.

On the basis of the total number of bands observed, structure (1) may be ruled out, and this elimination is in agreement with the electric-deflection work [12] since this structure would not possess a permanent dipole. Certain other structures also appear unlikely on the basis of relative band intensities and/or inequivalent oxygen

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[26] I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc.* (*A*), 1971, 2240.

atoms, and these arguments may now be presented in the context of band assignments.

TABLE 2

Vibrational spectra (cm^{-1}) of ReF_3O_2. Band accuracy ±0.5 cm^{-1} in i.r., ±1.0 cm^{-1} in Raman

Observed frequencies] (N_2 matrix) I.r.	Observed frequencies] (N_2 matrix) Raman	Observed frequencies (Ar matrix) I.r.	Observed frequencies (Ar matrix) Raman	Mode	Description
1 029m	1 029vs	1 024.2m	1 026vs	ν_1 a_1	ReO_2 sym str.
701s	701s	703, 704s *	703s	ν_2 a_1	ReF_{eq} str.
	368m		370m	ν_3 a_1	ReO_2 scissor
621w	619m	622, 623w *	621m, br	ν_4 a_1	ReF_2 sym str.
	326m		326m	ν_5 a_1	ReF_2 sym scissor
(Inactive)	360m	(Inactive)	357m	ν_6 a_2	torsion
674s		677s		ν_7 b_1	ReF_2 asym str.
286mw	288vw	287mw	*ca.* 290vw	ν_8 b_1	ReO_2 wag
252w	*ca.* 250vvw	251w	*ca.* 250vvw	ν_9 b_1	ReF_2 asym in-plane scissor
992s	991w	988.4s	990w	ν_{10} b_2	ReO_2 asym str.
271w	273vw	272w	272vw	ν_{11} b_2	ReO_2 rock
260w	262vw	260w	262vw	ν_{12} b_2	ReF_2 out-of-plane scissor

* Matrix site effect.

The following internal force constants reproduce the argon-matrix frequencies exactly (see text for definitions of angles and molecular geometry):

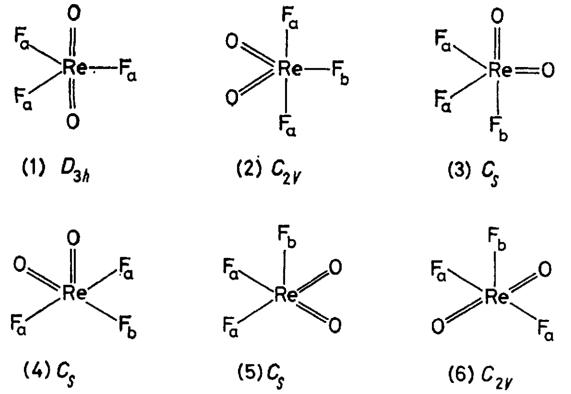
$$\left.\begin{array}{rr} f_D & 8.748 \\ f_R & 5.041 \\ f_r & 4.284 \\ f_{DD} & 0.403 \\ f_{rr} & 0.055 \end{array}\right\}\text{mdyn Å}^{-1} \qquad \left.\begin{array}{rr} f\alpha & 1.173 \\ f\beta & 1.855 \\ f\gamma & 0.720 \\ f\delta & 1.209 \end{array}\right\}\text{mdyn Å rad}^{-2}$$

$$\left.\begin{array}{rr} f_{\beta\delta} = -f_{\beta\delta'} & 0.084 \\ f_{\gamma\delta} & -0.141 \\ f_{\beta\beta} & 0.945 \\ f_{\delta\delta} = -f_{\delta\delta'} & -0.229 \end{array}\right\}\text{mdyn Å rad}^{-2}$$

where	
$\beta\delta$	common F_a
$\beta\delta'$	no common atom
$\gamma\delta$	common O
$\delta\delta$	common F_a
$\delta\delta'$	common O

The remaining interaction constants were set at zero.

If one considers first the nitrogen-matrix results in the Re–O stretching region, it is evident that the bands at 1 029 cm^{-1} (i.r. medium, Raman very strong) and 992 cm^{-1} (i.r. strong, Raman weak) are symmetric and antisymmetric modes respectively of an ReO_2 unit, and from the relative intensities of these bands in the i.r. it is possible to estimate that the O–Re–O angle is *ca.* 100°. This estimate is based on the approximate relation * $I(\text{sym.})/I(\text{antisym.}) = \cot^2(\alpha/2)$ (where α is the angle O–Re–O) which will be expected to hold fairly well here since the rhenium atom is heavy in comparison with both oxygen and fluorine.


(1) D_{3h} (2) C_{2v} (3) C_s

(4) C_s (5) C_s (6) C_{2v}

Selection-rule data

Structure (symmetry)	(1) (D_{3h})	(2), (6) (C_{2v})	(3)—(5) (C_s)	Observed
Number of distinct fundamentals	8	12	12	12
Number of i.r. bands	5	11	12	9
Number of Raman bands	6	12	12	11
Number of coincidences	3	11	12	8

FIGURE 3 Possible structures for ReF_3O_2

Three bands are found in the 600—750 cm^{-1} region characteristic of heavy metal–fluorine stretching vibrations. Structures (2)—(6) all have one unique fluorine atom F_b and two equivalent fluorine atoms F_a and thus three bands are expected in this region for all the five structures. Two of these will be totally symmetric, involving F_b and $2F_a$, and one antisymmetric, involving only $2F_a$, and a satisfactory assignment which takes note of the relative Raman intensities of symmetric and antisymmetric modes is therefore to identify the band at 674 cm^{-1} (i.r. strong, Raman not observed) as the antisymmetric mode. The remaining bands at 701 cm^{-1} (i.r. strong, Raman strong) and *ca.* 620 cm^{-1} (i.r. weak, Raman medium) are then assigned as the two symmetric modes involving fluorine atoms F_b and $2F_a$ respectively. Consideration of the relative i.r. intensities for the symmetric and antisymmetric vibrations of the $Re(F_a)_2$ unit in the expression above now suggests that the angle F_a–Re–F_a is 140°. This estimate ignores intensity borrowing by the symmetric $Re(F_a)_2$ mode from the unique Re–F_b vibration which lies only 80 cm^{-1} away, and is therefore likely to be a *lower* limit for the angle. Indeed, the absorption pattern in this region bears a strong resemblance to that observed for the T-shaped molecules ClF_3 and BrF_3 [27] with regard to both frequency and relative i.r. intensity (Table 3).

On the basis of the observed intensity patterns in the

* See later discussion.

[27] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 1971, **54**, 344.

Re–O and Re–F stretching regions, we therefore retain as most probable structures those models which possess significantly bent ReO_2 units and approximately T-*shaped* ReF_3 groups, and for this reason eliminate structures (3), (5), and (6). A choice thus remains between (2) and (4), which can in principle be resolved if it can be shown that the two oxygen atoms in ReF_3O_2 are equivalent and the ^{18}O-enrichment experiments described below were carried out with this end in view. These experiments strongly suggest equivalent oxygen atoms, and for this reason we believe that structure (2), with C_{2v} symmetry, is the most reasonable model on which to base our vibrational assignments. For this geometry, $\Gamma_{vib} = 5a_1 + a_2 + 3b_1 + 3b_2$ with $\Gamma_{stretch} = 3a_1 + b_1 + b_2$, and from the discussion above, the stretching modes may be identified as: 1 029, a_1; 992, b_2; 701, a_1; 674, b_1; and 620 cm^{-1}, a_1. Assignment of the bending frequencies is not as clear-cut. Four bands are found in the i.r. spectra (286, 271, 260, and 252 cm^{-1}) which have very weak counterparts in the Raman, and we assign these to the antisymmetric deformations $2b_1 + 2b_2$. Three comparatively intense bands are found in the Raman (368, 260, and 326 cm^{-1}) for which we could find no i.r. counterparts. The a_2 mode is formally inactive in the i.r., and the two remaining a_1 bending modes might be expected to have low i.r. intensities. In view of the possibility of interaction between these two a_1 modes, we believe it unlikely that both the bands at 368 and 360 cm^{-1} are in the same a_1 symmetry class, and thus assign the band at 326 cm^{-1} as an a_1 mode. From our results we are unable to distinguish the remaining a_1 and a_2 bending modes, and there is no *a priori* method of differentiating between b_1 and b_2 vibrations in the bending regions. Table 2 summarises what we believe to be a plausible assignment for these bands together with an approximate description of each mode. The numbering scheme used by Christe and Curtis [28] for the isostructural molecule ClF_3O_2 has been retained here. The descriptions of some of these vibrations can only be approximate in view of the proximity of fundamentals in the low-frequency region.

TABLE 3

Observed bands (cm^{-1}) and relative i.r. intensities for the stretching modes of some C_{2v} MF_3 units

Mode		$^{35}ClF_3$ [a]	$^{79}BrF_3$ [a]	ReF_3O_2 [b]
MF str.	a_1	754.0s	678.1s	701s
MF_2 asym str.	b_1	683.2vs	599vs	674s
MF_2 sym str.	a_1	523w	547w	621w

[a] Ref. 27, argon matrix. [b] This work, nitrogen matrix.

During the course of this work a number of experiments were carried out using relatively concentrated matrices and spectra from these deposits showed weak satellite bands in the Re–O stretching region in addition to ReF_3O_2 and $ReFO_3$ absorptions. These additional weak features were not examined in detail, but they were certainly not associated with the monomeric species discussed above. It is possible that they may be fundamentals of the dimer $Re_2F_6O_4$, but the relative intensity of these bands did not increase during diffusion studies. The only other minor complication arising from these spectra was an almost exact frequency overlap between the unique Re–F stretch in $ReFO_3$ (ν_1) and the equatorial Re–F stretch in in ReF_3O_2 (ν_2). This was initially detected by the anomalous intensity behaviour of the feature at 701 cm^{-1} present in nitrogen matrices and subsequently confirmed by independent experiments on $ReFO_3$ and by the separation of these two modes in argon matrices.

Vibrational analysis. A vibrational analysis for ReF_3O_2 was carried out assuming a trigonal-bipyramidal structure with equatorial oxygen atoms [structure (2), Figure 3]. The force field employed was similar to that derived by Christe and Curtis [28] in their analysis of ClF_3O_2, and the following molecular parameters were assumed: D(Re–O) 1.7; R(Re–F_b) 1.8; r(Re–F_a) 1.8 Å; α (angle O–Re–O) 100; β (F_b–Re–F_a) 85; and γ (O–Re–F_b) 130°. These angle parameters then determine a final angle parameter δ(O–Re–F_a) of 93.2°. As was the case for ClF_3O_2, the number of independent force constants is considerably larger than the number of observed frequencies, and our calculations were therefore carried out with the aim of reproducing the observed frequencies to within experimental error using a minimum of physically realistic parameters. This procedure inevitably involves several arbitrary assumptions, and in particular, since the five force constants f_D, f_{DD}, f_R, f_r, and f_{rr} contain sufficient flexibility to generate the five stretching frequencies, the interaction constants f_{DR} and f_{Dr} were set equal to zero. Data from ^{18}O studies was not included in the force-constant refinement, as it was our intention to use this additional information to assess the suitability of this force field. Table 2 compares the frequencies observed for ReF_3O_2 in N_2 and argon matrices, and lists the values of the 13 force constants used to reproduce the argon-matrix frequencies. Apart from the value of $f_{\beta\beta}$ which is rather larger than expected, the interaction constants are considerably lower than the principal constants, and the values of f_D, f_R, and f_r are very reasonable by comparison with $ReFO_3$ and ClF_3O_2.[28] In particular, it appears from the high value of f_D that the rhenium–oxygen bond in ReF_3O_2 contains appreciable double-bond character and the values for f_R and f_r indicate that the equatorial Re–F bond is perhaps stronger and shorter than the bonds to the axial fluorines.

^{18}O-*Enrichment Studies.*—One important difference between structures (2) and (4) concerns the equivalence of the two oxygen atoms, and samples of ^{18}O-enriched ReF_3O_2 were prepared in an attempt to discover whether two structural isomers exist for the partially substituted species $ReF_3{}^{16}O^{18}O$. As noted earlier, $ReFO_3$ is a persistent impurity in this system, but rather than attempt to remove this impurity from our ^{18}O samples we chose instead to vary its proportion in a predictable manner so that we would obtain additional ^{18}O data for $ReFO_3$ and at the same time be able to distinguish between the isotope patterns for $ReFO_3$ and ReF_3O_2.

Typical i.r. spectra obtained from ^{18}O-enriched samples of ReF_3O_2 are shown in Figure 4. Figure 4(*a*) shows an

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[28] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 1973, **12**, 2245.

argon-matrix survey spectrum and is included here to indicate that, whereas the Re–O stretching region is quite complicated, the Re–F stretching region remains almost identical to that found without enrichment (Figure 2). Spectrum (*b*) shows the Re–O stretching region of (*a*) under higher scale expansion, whilst (*d*) was recorded under similar conditions to (*b*) but with a greater proportion of $ReFO_3$. The line spectra (*c*) and (*e*) show the results of frequency and intensity calculations on ReF_3O_2 and $ReFO_3$, and the frequency data for spectra (*b*)–(*e*) appear in Table 4.

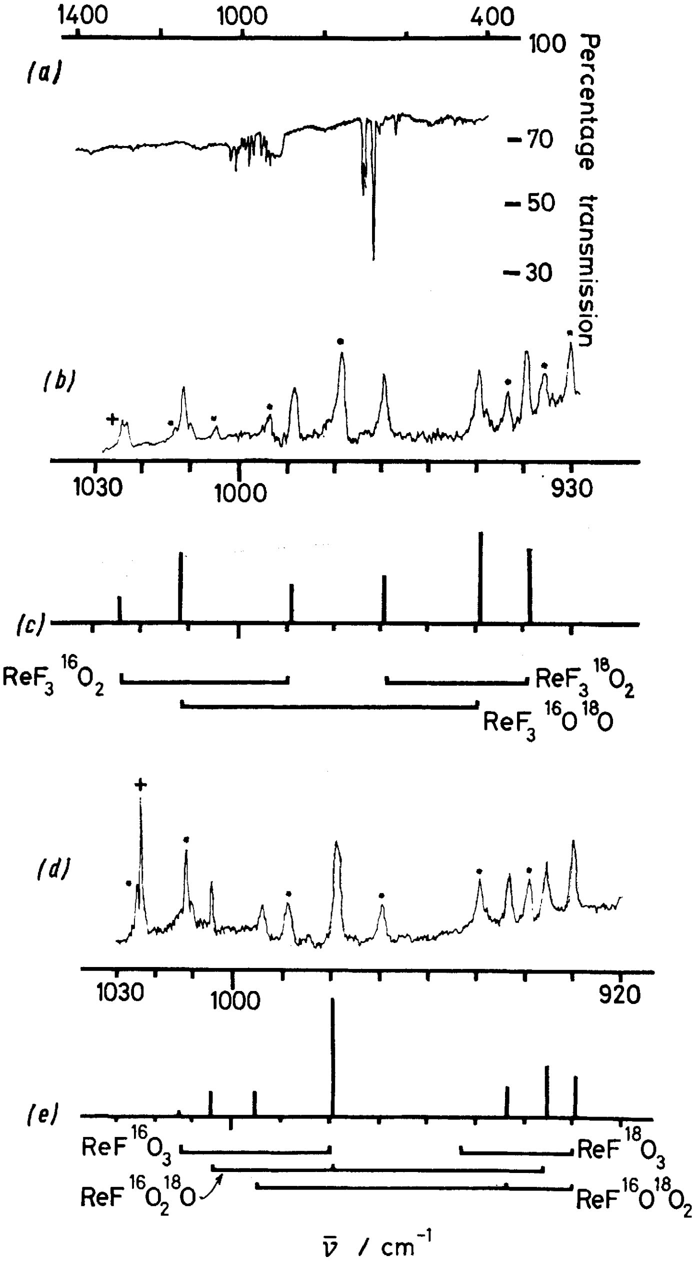

FIGURE 4 Infrared spectra of matrix-isolated ReF_3O_2 and $ReFO_3$ with ^{18}O enrichment: (*a*) typical low-resolution spectrum; (*b*) high resolution, (+) band due to matrix-isolated SiF_4, (*) bands due to matrix-isolated $ReFO_3$; (*c*) calculated spectrum for ^{18}O-enriched ReF_3O_2; (*d*) high resolution, (+) band due to matrix-isolated SiF_4, (*) bands due to matrix-isolated ReF_3O_2; (*e*) calculated spectrum for $ReFO_3$

These results were interpreted using a force-constant analysis similar to that previously employed in our earlier interpretation of ^{18}O-enriched OsF_2O_3.[4] In particular, we assume that the isotope patterns for ReF_3O_2 and $ReFO_3$ may be analysed by treating the Re–O stretching region of the spectrum in terms of a bent ReO_2 and a pyramidal ReO_3 unit respectively. *G* and *F* matrices are derived based on the lowest symmetry unit encountered (*i.e.* C_s) and three independent parameters (a principal Re–O stretching constant, an interaction constant, and the O–Re–O angle) are retained for each molecule. The use of only one principal Re–O stretching constant is equivalent to assuming that the Re–O bonds are identical, and the validity of this assumption for ReF_3O_2 is tested by noting the total number of bands assigned to ReF_3O_2 in this region. For a bent ReO_2 unit, each isotopically distinct molecule will give two i.r.-active bands, and since only six are observed these can only reasonably be assigned to $Re^{16}O_2$, $Re^{18}O_2$, and a single mixed species $Re^{16}O^{18}O$. $ReFO_3$ is known to have C_{3v} symmetry, and the angle O–Re–O = 109.5° derived from the microwave study may be used, but in the case of ReF_3O_2 it is necessary to obtain an estimate for this angle from the spectrum.

As indicated earlier, such an estimate is available from the relative intensities of the symmetric and antisymmetric Re–O stretching modes if these vibrations are effectively uncoupled from the other modes in the molecule, and the relation $I(a_1)/I(b_2) = \cot^2(\alpha/2)$ for the ReO_2 unit yields a value of $100 \pm 5°$. Some indication of the reliability of this estimate may be gained by using a similar intensity relation to estimate the bond angle in the ReO_3 pyramid from our spectra. Here, the relevant intensity quotient is $I(a_1)/I(e)$ for the Re–O stretching modes, and this ultimately yields a value of $110 \pm 7°$ which compares quite favourably with the microwave value. This approach will in general be useful if the off-diagonal *G* and *F* matrix elements relating these stretching modes to other modes of the same symmetries are small, but three further conditions should also be satisfied if these bond-angle values and the subsequent isotope-intensity calculations are to be taken seriously. First, one must assume that the changes in overall molecular dipole which take place as a result of these vibrations can be expressed as vector sums of bond-dipole changes along the Re–O bonds. Secondly, since ReF_3O_2 (C_{2v}) will possess a permanent dipole, one must assume that coupling with rotational motion is negligible, and, finally, one assumes that the double-harmonic approximation is true. These qualifications have been discussed by Burdett *et al.*[29] primarily in connection with the use of isotope-frequency and intensity patterns in carbonyl chemistry, but they will apply, in general, to any system.

It is impossible to assess the extent to which all these

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[29] J. K. Burdett, M. Poliakoff, J. J. Turner, and H. Dubost, 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden and Son, London, 1976, vol. 2.

approximations will be valid for a hitherto uncharacterised species. However, our success [4] in interpreting similar frequency and intensity patterns in the related molecules OsO_4 and OsF_2O_3 suggests that this approach may usefully be applied here to both ReF_3O_2 and $ReFO_3$, where the presence of a heavy central atom once again effectively ensures that G-matrix coupling at least will be minimised.

The results displayed in Figure 4 and Table 4 are almost self-explanatory. Six bands are observed for ^{18}O-enriched ReF_3O_2 in this region of the spectrum, and these are adequately reproduced by a bent (100°) ReO_2 unit in which the principal Re–O stretching constant f_D and the interaction constant f_{DD} are given values of 8.805 and 0.425 mdyn Å^{-1} respectively. These parameters are very similar to those obtained from the more general force field (Table 2) and Table 4 also includes, for comparison, the frequencies predicted in this region for these isotopically substituted species using the 13-parameter force field described earlier. This agreement is also very satisfactory. For the relative-intensity calculations the statistical weights of the three isotopomers were obtained from the $^{16}O : {}^{18}O$ ratio employed in the preparation. Rhenium fluoride trioxide was similarly treated as a pyramidal ReO_3 unit with an interbond angle of 109.5° and with corresponding parameters F_R and F_{RR}. Frequency calculations predict a total of eight distinct bands in this region, but experimentally only seven are observed, and this is due to to non-random statistical weighting. The compound $ReFO_3$ is produced in these experiments by reaction between ReF_3O_2 and borosilicate glass, which is effectively an infinite source of ^{16}O. As a result the proportions of isotopically labelled $ReFO_3$ species are obtained by considering the addition of one ^{16}O atom to the existing ReF_3O_2 species, and, in particular, no $ReF^{18}O_3$ is produced. This absence is most noticeable for the a_1 mode predicted at *ca.* 957 cm^{-1}, but may also be inferred from the somewhat lower intensity observed for the band at 930 cm^{-1} than would be expected from an overlap of (e) $ReF^{18}O_3$ and (a'') $ReF^{16}O^{18}O_2$. The occurrence of these band overlaps in pyramidal and planar MX_3 systems has been discussed elsewhere [30] and will not be repeated here. Once again the force constants employed in the simplified analysis are very similar to those in the more general force field (Table 1), and the frequencies of isotopically substituted $ReFO_3$ molecules calculated from the latter are in good agreement with those found experimentally. These ^{18}O studies therefore support our claim concerning the origin of $ReFO_3$ in this work.

TABLE 4

Observed and calculated wavenumber (cm^{-1}) for ^{18}O-enriched $ReFO_3$ and ReF_3O_2

$ReFO_3$					ReF_3O_2				
Observed (Ar matrix)	Calculated		Assignment		Observed (Ar matrix)	Calculated		Assignment	
	(A) [a]	(B) [b]				(A) [c]	(B) [d]		
1 013.2	1 013.0	1 013.2	a_1	$ReF^{16}O_3$					
1 004.9	1 004.8	1 004.9	a'	$ReF^{16}O_2{}^{18}O$	1 024.2	1 024.2	1 024.2	a_1	$ReF_3{}^{16}O_2$
993.8	994.8	994.7	a'	$ReF^{16}O^{18}O_2$	1 011.6	1 011.6	1 011.5	a'	$ReF_3{}^{16}O^{18}O$
978.3	979.0	978.3	e	$ReF^{16}O_3$	988.4	989.4	988.4	b_2	$ReF_3{}^{16}O_2$
	979.0	978.3	a''	$ReF^{16}O_2{}^{18}O$	969.6	969.6	971.1	a_1	$ReF_3{}^{18}O_2$
	956.7	957.5	a_1	$ReF^{18}O_3$ [e]	949.4	949.1	949.0	a'	$ReF_3{}^{16}O^{18}O$
943.2	943.0	943.0	a'	$ReF^{16}O^{18}O_2$	939.2	938.1	937.4	b_2	$ReF_3{}^{18}O_2$
935.8	935.0	934.8	a'	$ReF^{16}O_2{}^{18}O$					
930.0	928.9	928.5	a''	$ReF^{16}O^{18}O_2$					

[a] Calculation (A) based on ReO_3 unit: $F_R = 8.556$ mdyn A^{-1}, $F_{RR} = 0.433$, interbond angle = 109.5°. [b] Calculation (B) uses force field described in Table 1. [c] Calculation (A) based on ReO_2 unit: $f_D = 8.805$ mdyn Å^{-1}, $f_{DD} = 0.425$, interbond angle = 100°. [d] Calculation (B) uses force field described in Table 2. [e] No contribution to the observed pattern from this molecule (see text).

Finally, our spectra for ReF_3O_2 have been interpreted on the basis of a C_{2v} structure, and it is of some interest to test this assumption by estimating the degree of *inequivalence* between the two oxygen atoms which could theoretically be detected from our ^{18}O studies. Equivalent oxygen atoms in a bent MO_2 unit will, on 50% ^{18}O enrichment, yield two *triplets* with components of approximate relative intensity 1 : 2 : 1. A species MOO′ with inequivalent oxygen atoms would be expected to have two different primary stretching constants, and could in principle be identified by the occurrence of two *quartets*, in which the components have approximate relative intensity 1 : 1 : 1 : 1. It is therefore necessary to estimate how different the primary MO and MO′ stretching constants have to be to observe a detectable splitting of the central components of our two triplets.

First, we note that the bands we assign to $ReF_3{}^{16}O^{18}O$ are *ca.* 1.5—2.0 cm^{-1} wide, and are no wider than those of $ReF_3{}^{16}O_2$ or $ReF_3{}^{18}O_2$: we estimate that any possible splitting greater than 1 cm^{-1} would be detected. In order to study the problem quantitatively, a small perturbation was introduced into the two-parameter force field for ReF_3O_2 such that the Re–O force constants were given values $f_D + f_\Delta$ and $f_D - f_\Delta$, where f_Δ was varied between 0.0 and 0.05 mdyn Å^{-1}. The original value of f_{DD} was retained. This perturbation ensures that the central components of our triplets will split into equal doublets, whilst leaving our $Re^{16}O_2$ and $Re^{18}O_2$ bands essentially unaffected. Theoretical splittings $\Delta\nu$ were then calculated for each value of f_Δ and some typical results are:

f_Δ/mdyn Å^{-1}	0.00	0.01	0.02	0.03
$\Delta\nu$/cm^{-1}	0.0	1.0	1.9	2.9

It is therefore evident that a very small difference in primary Re–O force constants (*ca.* 0.2%) would be expected to give rise to perceptible broadening or splitting

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[30] I. R. Beattie, H. E. Blayden, S. M. Hall, S. N. Jenny, and J. S. Ogden, *J.C.S. Dalton*, 1976, 606.

of the bands assigned to $ReF_3{}^{16}O^{18}O$. No such evidence was observed, and we believe that these experiments provide excellent justification for the equivalence of the oxygen atoms in ReF_3O_2.

Conclusions.—On the basis of these experiments, we conclude that rhenium trifluoride dioxide sublimes primarily as a monomer, and that molecular ReF_3O_2 has C_{2v} symmetry with a geometry based on the trigonal bipyramid. These results make an interesting contrast with the related IF_3O_2 system, where oxygen-bridged dimers predominate in the vapour phase.[3,6] In an earlier rationalisation,[3] which drew attention to a corresponding difference between WF_4O (essentially a monomeric vapour) and TeF_4O (*dimeric* in the vapour phase), it was suggested that the principal reason for this structural difference was that for the d^0 species the chemistry is dominated by strong oxygen–metal p_π–d_π bonding, whereas the capacity for multiple-bond formation involving the heavier *p*-block elements is much less. This theory also appears to be relevant here.

It is also interesting to compare the C_{2v} geometry derived here for ReF_3O_2 with heavier d^2 transition-metal dioxo-species where the formation of *linear* MO_2 groups seems to be strongly favoured.[31] Many of these linear systems are well characterised structurally, and it would clearly be of interest to carry out a microwave or electron-diffraction study on ReF_3O_2 both to confirm our conclusions regarding C_{2v} symmetry and to obtain accurate structural information. It is also clear that the structure of ReO_2Me_3 deserves detailed examination in view of the claim[7] that this molecule contains *inequivalent* oxygen atoms. This conclusion was based on n.m.r. data in solution but has not been confirmed for the vapour phase.

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[7/019 *Received, 5th January*, 1977]

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[31] F. A. Cotton, *Proc. Climax 1st Internat. Conf. Chem. Uses of Molybdenum*, September, 1973; W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 211; K. H. Schmidt and A. Müller, *Co-ordination Chem. Rev.*, 1974, **14**, 15.