Spectroscopic Studies on the Hexafluorides of Ruthenium and Rhodium isolated in Low-temperature Matrices†

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New syntheses of RuF_6 and RhF_6 are reported involving fluorination of the corresponding pentafluorides at 220 °C and 30 atm. Infra-red spectra for RuF_6 and RhF_6 isolated in nitrogen and argon matrices at 12 K have been recorded and assigned. The u.v.–visible spectra in nitrogen matrices are complex containing both fluorine-to-metal charge-transfer and *d–d* transitions. Assignments for the main features are proposed.

The 4*d* platinum-group hexafluorides RuF_6 and RhF_6 are the least stable and least studied of all the known hexafluorides. However, since they are practically the only examples of neutral molecules in these high oxidation states, their spectroscopic characterisation is of particular interest.

The limited information available on these species is a direct result of their instability: RhF_6 is reported to decompose rapidly at room temperature,[1] whilst RuF_6 is stable at room temperature only in pre-passivated nickel containers.[2] Consequently the only syntheses of these molecules involve quenching the reaction products to low temperatures to avoid decomposition: for example, burning a metal wire in a fluorine atmosphere in a quartz reactor immersed in liquid nitrogen[1,3] or, for Ru alone, the high-temperature fluorination of ruthenium powder in a sealed reactor with the upper surface cooled to −78 °C.[2] Both molecules are monomeric in the gas phase and, on the basis of i.r. data[1,3] and electric deflection measurements,[4] possess octahedral symmetry.

As part of our continuing research programme on binary transition-metal fluorides,[5] this paper describes new preparative routes and detailed spectroscopic studies of RuF_6 and RhF_6 isolated in inert-gas matrices. The matrix-isolation technique allows high-resolution spectroscopic studies of extremely reactive materials with minimal corrosion and containment problems.

Experimental

The compounds RuF_6 and RhF_6 were prepared in high yield by static fluorination of the corresponding pentafluorides, which were made by literature methods.[6,7]

In a typical preparation, a Monel autoclave (300 cm^3) was charged in a dry-box with powdered RuF_5 (0.5 g, 2.6 mmol) and evacuated. Fluorine gas (9 l, 1 atm) was condensed into the autoclave at −196 °C *via* a metal vacuum line, the autoclave sealed, and warmed slowly to room temperature, affording a starting pressure of *ca.* 30 atm. The autoclave was heated by an external furnace to 230 ± 20 °C for 72 h. After this time the autoclave was cooled to room temperature, and then to −196 °C with liquid nitrogen. It was slowly warmed to −110 °C (methanol slush) and the excess of fluorine removed. The autoclave was then filled with dry nitrogen or argon to *ca.* 1 atm. In several cases after removal of materials volatile at room temperature, the autoclave was opened in a glove-box and little or no involatile products were found (the pentafluorides have very small volatilities at room temperature even *in vacuo*). Under these conditions conversion into the brown RuF_6 and dark red RhF_6 occurs in high yield.

The general features of the matrix-isolation equipment used for our spectroscopic studies have been described elsewhere.[8] In this work RuF_6 and RhF_6 were sprayed into the matrix rig directly from the autoclave (maintained at −5 and −40 °C respectively) *via* a stainless-steel tube pre-passivated with fluorine. Both nitrogen and argon (B.O.C. >99.99%) were used as matrix gases. I.r. studies were carried out using a Perkin-Elmer PE 983G spectrometer with the matrix rig fitted with CsI optics, and u.v.–visible studies on a Perkin-Elmer 554 spectrometer interfaced with a microcomputer and using LiF optics. Matrix ratios were estimated to be in excess of 1 000:1. Attempts to record mass spectra using electron-impact ionisation led only to the observation of strong $[WF_{6-n}]^+$ (n = 0—6) ions, due to rapid corrosion of the tungsten filament.

Results and Discussion

Synthesis.—This new synthesis involving static fluorination of the corresponding pentafluorides at *ca.* 220 °C and a working pressure of *ca.* 50—60 atm, is much more convenient than the previous methods, in that it involves no specially designed apparatus. It produces the hexafluorides in yields which will allow their reaction chemistries to be explored, and permit their use as starting materials for the attempted synthesis of presently unknown high-valent fluoride oxides and derivatives. Contrary to previous reports that RhF_6, in particular, decomposes rapidly at room temperature, we found that decomposition at room temperature of RhF_6 in the autoclave was minimal over the several days used for the matrix-isolation studies. It seems possible that the previously reported 'thermal' instability of these compounds at temperatures near ambient is in part a reflection of their extremely aggressive nature and the ease with which they attack most materials. In our studies they were stored in the autoclave in which they were synthesised, which is clearly 'passivated' with respect to attack by the MF_6.

I.R. Spectroscopic Studies.—The vibrational fundamentals of both RuF_6 and RhF_6 in the gas phase have been reported previously.[9,10] Both molecules adopt O_h symmetry and are thus expected to exhibit two i.r.-active fundamentals of T_{1u} symmetry. The spectra of our compounds were recorded using both nitrogen and argon as matrix gases, but the nitrogen

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. Principal i.r. absorptions (cm^{-1})

Compound	Gas phase[a]	Nitrogen matrix[b]	Argon matrix[b]	Assignment
RuF_6	735	731.6/725.7	731.3	ν_3 (T_{1u} stretch)
	275	273.0	—	ν_4 (T_{1u} bend)
RhF_6	724	720.1	723.2	ν_3 (T_{1u} stretch)
	284	288.3	287.8	ν_4 (T_{1u} bend)

[a] Ref. 10. [b] This work: frequency accuracy ±0.5 cm^{-1}.

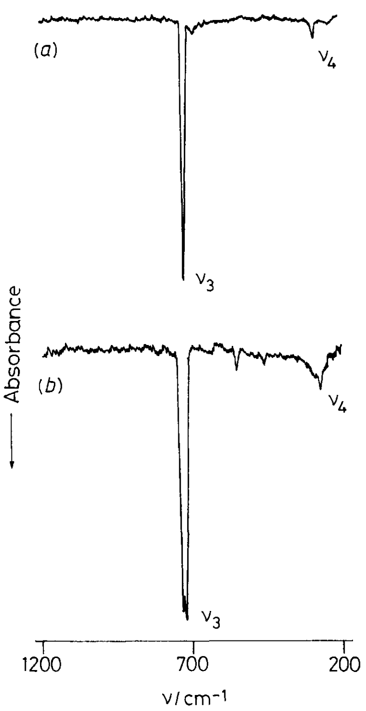

Figure 1. I.r. spectra of (*a*) RhF_6 and (*b*) RuF_6 isolated in nitrogen matrices

matrices consistently yielded superior quality spectra, and hence the majority of the results refer to species isolated in nitrogen matrices. When samples of RhF_6 were matrix isolated subsequent survey spectra revealed two absorptions, centred at 720.1 and 288.3 cm^{-1} [nitrogen matrix, Figure 1(*a*)] and 723.2 and 287.8 cm^{-1} (argon matrix). These absorptions correlate well with the gas-phase spectrum as shown in Table 1 and, moreover, demonstrate that the RhF_6 was essentially free of impurity. However, when RuF_6 was similarly cocondensed with an excess of nitrogen a total of ten bands was observed. The most intense feature was at *ca.* 730 cm^{-1} with additional much weaker features at *ca.* 922, 746, 722, 710, 661, 552, 470, 313, and 273 cm^{-1}. The highest-frequency absorption at 922.4 cm^{-1} ceased to grow after the first few depositions, and its occurrence could normally be prevented by pretreating the spray-on system with RuF_6 vapour before cool down. This behaviour is typical of a hydrolysis product,[5] and by comparison with the published gas-phase spectrum this band is assigned to RuO_4 which shows [11] ν_3 at 921 cm^{-1}.

Spectral subtractions between successive depositions demonstrated that the bands at *ca.* 730 and 273 cm^{-1} grew independently of the other absorptions, and it was possible to obtain spectra dominated by these two features [Figure 1(*b*)] using short pulsed depositions, rather than slow spray-on conditions. These bands lie very close to the frequencies of the gas-phase fundamentals of RuF_6,[10] and are thus assigned to the T_{1u} modes of molecular RuF_6. The remaining weaker features are provisionally assigned to decomposition products of RuF_6, presumably lower binary fluorides. Studies on vapour-phase RuF_5 and RuF_4 are in progress which may allow identification of these weak features.

Examination of the T_{1u} stretching mode of RhF_6, in both nitrogen and argon matrices under high resolution, revealed no fine structure. In contrast, the stretching mode of RuF_6 in nitrogen, recorded under similar conditions, appeared as two components of approximately equal intensity, at 731.6 and 725.7 cm^{-1}. This splitting (*ca.* 5.9 cm^{-1}) is too large to be accounted for by ruthenium isotope effects and may be due either to a lifting of the degeneracy of the T_{1u} mode by the matrix environment, as observed previously with other platinum-metal hexafluorides,[5] or it could be the result of a Jahn–Teller distortion.[10]

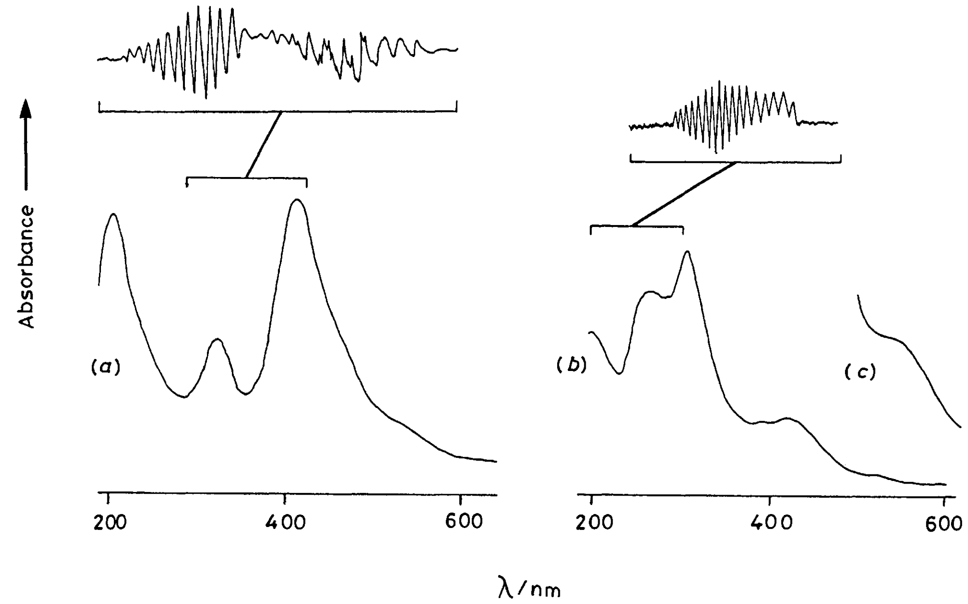

Figure 2. U.v.–visible spectra of (*a*) RhF_6 and (*b*) RuF_6 isolated in nitrogen matrices; the vibrational structure observed by second-derivative recording is shown above appropriate bands; (*c*) shows the spectrum of RuF_6 after extended deposition

Table 2. U.v.–visible data[a]

Compound	$E_{max.}$/cm^{-1} (Δ/cm^{-1})[b]	Assignment
MoF_6	46 000(sh)[c]	$\pi(F) \longrightarrow t_{2g}(Mo)$
	53 000(630)	$\pi(F) \longrightarrow t_{2g}(Mo)$
RuF_6	*ca.* 1 400[d]	$^3T_{1g}(\Gamma_3,\Gamma_5) \longrightarrow {}^3T_{1g}(\Gamma_4)$
	ca. 1 950[d]	$^3T_{1g}(\Gamma_3,\Gamma_5) \longrightarrow {}^3T_{1g}(\Gamma_1)$
	18 400(sh)	$^3T_{1g} \longrightarrow {}^1A_{1g}$
	23 680	$^3T_{1g} \longrightarrow {}^3T_{2g}$
	25 600(sh)	$\pi(F) \longrightarrow t_{2g}(Ru)$
	32 800	$\pi(F) \longrightarrow t_{2g}(Ru)$
	37 940(600)	$\pi(F) \longrightarrow t_{2g}(Ru)$
	$>$51 000	$\pi(F) \longrightarrow e_g(Ru)$ or $\sigma(F) \longrightarrow t_{2g}(Ru)$
RhF_6	18 650(sh)	$^4A_{2g} \longrightarrow {}^2T_{2g}$
	22 550(sh)	$\pi(F) \longrightarrow t_{2g}(Rh)$
	24 250(580)	$\pi(F) \longrightarrow t_{2g}(Rh)$
	30 850(530)	$\pi(F) \longrightarrow t_{2g}(Rh)$
	49 000	$\pi(F) \longrightarrow e_g(Rh)$ or $\sigma(F) \longrightarrow t_{2g}(Rh)$

[a] Nitrogen matrices. [b] Average vibrational progressions ±30 cm^{-1}. [c] Data from R. McDiarmid, *J. Chem. Phys.*, 1974, **61**, 3333. [d] Data from ref. 10.

These i.r. studies thus established the conditions under which the compounds RuF_6 and RhF_6, free of contamination, could be isolated in low temperature matrices. I.r. spectra were generally recorded immediately prior to the u.v.–visible studies, and in most cases also immediately afterwards, to check the sample integrity.

U.V.–Visible Spectroscopic Studies.—Electronic spectra were recorded over the range *ca.* 190—900 nm (52 000—11 000 cm^{-1}) for RuF_6 and RhF_6 isolated in nitrogen matrices at 12 K. Some data were also obtained in argon matrices, but the quality was higher in nitrogen. Nitrogen-matrix data are presented in Table 2 and typical spectra are shown in Figure 2. Several spectra were recorded for each sample, and for RhF_6 reproducibility between runs was excellent. For RuF_6 initial depositions gave spectra which contained features characteristic of RuF_6 (below) and RuO_4, the latter producing two strong, highly structured features at *ca.* 26 500 and *ca.* 33 100 cm^{-1} with vibrational progressions of *ca.* 800 cm^{-1}. These data correlate well with the gas-phase spectrum.[12] Difference spectra recorded after subsequent depositions showed no evidence of RuO_4, and samples deposited after the apparatus had been thoroughly passivated with RuF_6 vapour were similarly free of the impurity. Spectroscopic studies of OsF_6 and osmium fluoride oxides, are similarly complicated by the ubiquitous appearance of OsO_4.[5,13]

Previous assignments[5,14] of the spectra of the 5*d* hexafluorides WF_6 to PtF_6 identified three types of transition: charge transfer (π or σ)F $\longrightarrow$ (t_{2g} or e_g)M; *d–d* transitions between the t_{2g} and e_g levels; and intraconfigurational bands arising from a redistribution of electrons within the spin–orbit split t_{2g} levels. For the 5*d* elements the large spin–orbit coupling constants (ζ) require explicit inclusion of spin–orbit effects, but for the present 4*d* systems (ζ *ca.* 1 000 cm^{-1})[15] spin–orbit effects are unlikely to produce resolvable band splittings in the visible and u.v. regions although some intensity enhancement of spin-forbidden transitions may occur. Hence, for RuF_6 and RhF_6, the *d–d* transition assignments are based upon the Russell–Saunders scheme and the appropriate Tanabe–Sugano diagram.[16] Treatment of the charge-transfer transitions is not fundamentally different from that of the 5*d* analogues, and the observed energy of the lowest Laporte-allowed $\pi(F) \longrightarrow t_{2g}(M)$ transition may be treated by Jorgensen's relationship[14] $E_{max.} = V + KD + q(A - E)$ [*A*,*D* are related to the corresponding Racah parameters, *E* is the variation in orbital energy with the occupation number (*q*), and *V* and *K* depend upon the metal oxidation state and atomic number]. Alternatively, the optical electronegativity formula $E_{max.} = 30\,000\ [\chi_{opt}(F) - \chi_{opt}(M)]$ may be used after correction for spin pairing and, if desired, spin–orbit effects. Since $\chi_{opt}(M)$ can be used subsequently to predict the charge-transfer energies in other compounds of that oxidation state, it is the more useful approach.

The spectral data on RuF_6 ($4d^2$) and RhF_6($4d^3$) along with literature data on MoF_6 ($4d^0$) are listed in Table 2. No data are available for TcF_6 ($4d^1$) and its radioactivity precluded its inclusion in the present study.

MoF_6. The d^0 case exhibits only $\pi(F) \longrightarrow t_{2g}(Mo)$ charge-transfer transitions at 53 000 cm^{-1} with a vibrational structure of *ca.* 630 cm^{-1}, and a structureless shoulder at *ca.* 46 000 cm^{-1}. These are respectively assigned to Laporte allowed and forbidden transitions.

RuF_6. The spectrum in Figure 2 reveals two intense absorptions at 37 940 and 32 800 cm^{-1}, and a further strong feature appears to lie $>$51 000 cm^{-1} beyond the limit of the spectrometer. Weaker features are present at *ca.* 25 600(sh) and 23 680 cm^{-1} and, after extended deposition a much weaker feature appears as a shoulder at 18 400 cm^{-1}. The two intense features at 37 940 and 32 800 cm^{-1} are clearly allowed $\pi(F) \longrightarrow t_{2g}(Ru)$ transitions, and the higher-energy band shows a well defined vibrational progression of *ca.* 600 cm^{-1} which correlates with the A_1(Ru–F) mode at 675 cm^{-1} in the ground state.[9] The feature at 25 600 cm^{-1} is provisionally assigned as a parity-forbidden charge-transfer band. The intense feature $>$51 000 cm^{-1} is again charge transfer in type, but either $\pi(F) \longrightarrow e_g(Ru)$ or $\sigma(F) \longrightarrow t_{2g}(Ru)$ are possible assignments. For a d^2 ion in O_h symmetry three spin-allowed *d–d* transitions are predicted, in order of increasing energy $^3T_{1g} \longrightarrow {}^3T_{2g}$, $^3T_{1g} \longrightarrow {}^3A_{2g}$, and $^3T_{1g} \longrightarrow {}^3T_{1g}(P)$, and the feature at 23 680 cm^{-1} is assigned as $^3T_{1g} \longrightarrow {}^3T_{2g}$, the higher-energy bands being obscured by the more intense charge-transfer transitions. The weak shoulder at 18 400 cm^{-1} is then the spin-forbidden $^3T_{1g} \longrightarrow {}^1A_{1g}$ transition, and the other spin-forbidden bands expected $^3T_{1g} \longrightarrow {}^1E_{1g}$, $^1T_{1g}$ are probably in the near-i.r. region ($<$11 000 cm^{-1}) and were not observed. The data are clearly too limited for a detailed treatment, but can be approximately fitted to the Tanabe–Sugano diagram for a d^2 ion leading to $10Dq$ = *ca.* 27 000 cm^{-1}, *B ca.* 550 cm^{-1} (C/B = 4.4), which seem reasonable compared with $[RuF_6]^{2-}$ ($10Dq$ 25 000 cm^{-1}, B = 500 cm^{-1}) and $[RuF_6]^-$ ($10Dq$ = 26 000 cm^{-1}, B = 425 cm^{-1}).

Finally, we note that in their study of the gas-phase i.r. spectrum of RuF_6, Weinstock *et al.*[10] observed weak features at 1 400 and 1 950 cm^{-1} which are probably intraconfigurational transitions $\Gamma_3,\Gamma_5 \longrightarrow \Gamma_4$ (1 400 cm^{-1}) and $\Gamma_3,\Gamma_5 \longrightarrow \Gamma_1$ (1 950 cm^{-1}) within the split $^3T_{1g}$ ground state. In the absence of configurational interaction these levels are separated in energy by 2λ and 3λ respectively which leads to approximate values for λ = *ca.* 650 cm^{-1} and ζ = *ca.* 1 300 cm^{-1}, which seem reasonable compared to the estimated free-ion value[15] for $\zeta(Ru^{VI})$ = 1 700 cm^{-1}, and support the assignment. These bands were not observed in the much more dilute matrices in the present study.

RhF_6. The spectrum contains intense bands at 49 000, 30 850, and 24 250 cm^{-1}, the last two having vibrational progressions of *ca.* 530 and *ca.* 580 cm^{-1} respectively which correlate with the ground-state vibration A_{1g}(Rh–F) of 634 cm^{-1}. These two are assigned as $\pi(F) \longrightarrow t_{2g}(Rh)$ charge-transfer transitions. Weaker features at 22 550 and 18 650 cm^{-1} are also present. For a d^3 ion in O_h symmetry three spin-allowed transitions are expected, $^4A_{2g} \longrightarrow {}^4T_{2g}$, $^4A_{2g} \longrightarrow {}^4T_{1g}$, and $^4A_{2g} \longrightarrow$

${}^4T_{1g}$(P), of which the first corresponds to $10Dq$. From the reported $10Dq$ values of *ca.* 27 000 cm^{-1} for RuF_6 (above) and 26 000 cm^{-1} for the isoelectronic $[RuF_6]^-$ (data for $[RhF_6]^-$ are not available), it seems likely that $10Dq$ for RhF_6 will be $\geqslant$25 000 cm^{-1} and hence all the spin-allowed transitions will be obscured by charge-transfer bands. The feature at 22 550 cm^{-1} seems too low to be ${}^4A_{2g} \longrightarrow {}^4T_{2g}$, and is assigned as a further (parity-forbidden) charge-transfer band. The band at 18 650 cm^{-1} is assignable as the spin-forbidden ${}^4A_{2g} \longrightarrow {}^2T_{2g}$ transition. Although this appears a little high in energy in comparison with this band of $[RuF_6]^-$ (15 700 cm^{-1}), it is on the shoulder of an intense charge-transfer band, and this will have the effect of moving the apparent band maximum to higher energy. The only other bands which might be expected are the spin-forbidden ${}^4A_{2g} \longrightarrow {}^2T_{1g}, {}^2E_g$, which probably lie in the *near-i.r.* region, outside the range of the spectrometer. The ${}^4A_{2g}$ ground state transforms as Γ_8 in the O^* double group, but is not expected to split under spin–orbit effects in contrast to the ${}^3T_{1g}$ in RuF_6. The only unassigned band is that at 49 000 cm^{-1}, which is clearly charge transfer, but if $10Dq$ is *ca.* 25 000 cm^{-1} could be either $\pi(\text{F}) \longrightarrow e_g$ or $\sigma(\text{F}) \longrightarrow t_{2g}$, and a distinction between these is not possible on the available data.

χ_{opt} *and Some Comparisons.*—The optical electronegativity formula predicts the lowest-energy parity-allowed charge-transfer bands for RuF_6 and RhF_6 as in equations (1) and (2)

$$E_{\text{obs.}} = 30\,000[\chi_{\text{opt}}(\text{F}) - \chi_{\text{opt}}(\text{Ru})] - 4D/3 \qquad (1)$$

$$E_{\text{obs.}} = 30\,000[\chi_{\text{opt}}(\text{F}) - \chi_{\text{opt}}(\text{Rh})] + 2D \qquad (2)$$

respectively. The magnitude of the Racah parameter D is not known, but if we use $D = 7B$ and take $B = 550$ cm^{-1} from RuF_6 then these expressions give $\chi_{\text{opt}}(\text{Ru}^{\text{VI}})$ as 2.7 and $\chi_{\text{opt}}(\text{Rh}^{\text{VI}})$ as 3.3. In view of the approximations involved the values may be in error by ± 0.2 and, if spin–orbit effects were included, these would increase the value for Ru and decrease that for Rh (since they operate in opposite directions in d^2 and d^3 ions). If we compare the energies of the lowest-allowed $\pi(\text{F}) \longrightarrow t_{2g}(\text{M})$ charge-transfer transitions of MF_6 (M = Mo, 53 000; Ru, 32 800; Rh, 24 250; W, 64 000; Re, 47 000; Os, 36 000; Ir, 30 400; and Pt, 26 250 cm^{-1} [5]) we see that whereas towards the end of the $5d$ series the change with successive elements is *ca.* 4 000—5 000 cm^{-1}, in the $4d$ series it is approximately double that, reflecting the much greater ease of reduction of the later $4d$ hexafluorides.

Acknowledgements

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References

1 H. H. Claassen, H. Selig, J. G. Malm, C. L. Chernick, and B. Weinstock, *J. Am. Chem. Soc.*, 1961, **83**, 2390.
2 R. C. Burns and T. A. O'Donnell, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1613.
3 C. L. Chernick, H. H. Claassen, and B. Weinstock, *J. Am. Chem. Soc.*, 1961, **83**, 3165.
4 E. W. Kaiser, J. S. Muenter, W. Klemperer, W. E. Falconer, and W. A. Sunder, *J. Chem. Phys.*, 1970, **53**, 1411.
5 J. H. Holloway, G. Stanger, E. G. Hope, W. Levason, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 1341.
6 J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 527.
7 W. E. Falconer, G. R. Jones, W. A. Sunder, M. J. Vasile, A. A. Muenter, T. R. Dyke, and W. Klemperer, *J. Fluorine Chem.*, 1974, **4**, 213.
8 E. G. Hope, P. J. Jones, W. Levason, J. S. Ogden, M. Tajik, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1985, 1443.
9 H. H. Claassen, G. L. Goodman, J. H. Holloway, and H. Selig, *J. Chem. Phys.*, 1970, **53**, 341.
10 B. Weinstock, H. H. Claassen, and C. L. Chernick, *J. Chem. Phys.*, 1963, **38**, 1470.
11 R. S. McDowell, L. B. Asprey, and L. C. Hoskins, *J. Chem. Phys.*, 1972, **56**, 5712.
12 S. Foster, S. Felps, L. W. Johnson, D. B. Larsen, and S. P. McGlynn, *J. Am. Chem. Soc.*, 1973, **95**, 6578.
13 E. G. Hope, W. Levason, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 61, 997.
14 G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 1974, **19**, 105.
15 T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.
16 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984.

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