Matrix-isolation Infrared and Ultraviolet–Visible Studies on some Transition-metal Pentachlorides and Pentabromides

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Samples of the solids $NbCl_5$, $NbBr_5$, $TaCl_5$, $TaBr_5$, $ReCl_5$, $ReBr_5$ and $OsCl_5$ have been vaporised *in vacuo*, and the products characterised by mass spectrometry and IR and UV/VIS spectroscopy in low-temperature argon and nitrogen matrices. In particular it is shown that vaporisation of the d^0 species leads to the production of simple monomers, which adopt a square-pyramidal shape in nitrogen and a variety of conformers in argon. Rhenium pentachloride vaporises as a monomer which exhibits D_{3h} symmetry in both argon and nitrogen, but $ReBr_5$ and $OsCl_5$ decompose, the former to yield molecular Re_3Br_9.

In the solid state all the d-block pentachlorides and pentabromides are dimers with six-co-ordinate metal centres in edge-linked octahedra.[1–4] In contrast, the vapour species appear to be essentially monomeric, but their shapes are less clear. Electron diffraction studies on $NbCl_5$,[5] $TaCl_5$,[5] WCl_5[6] and $MoCl_5$[7] have been interpreted in terms of trigonal bipyramidal (D_{3h}) geometry, but more recently it has been proposed that $MoCl_5$ is a mixture of D_{3h} and C_{4v} monomers and a D_{4d} dimer.[8] It has also been suggested that the vapour species may undergo rapid D_{3h}–C_{4v} interconversion *via* a Berry-type mechanism.[9] Infrared and Raman studies on these pentahalide systems in the vapour phase have in general also favoured the trigonal-bipyramidal model,[10] but UV/VIS data have variously been interpreted in either C_{4v} or D_{3h} symmetry.[11,12]

All these studies have been carried out at elevated temperatures, where fluxional behaviour could easily give rise to an averaged structure showing relatively high symmetry. It is therefore of interest to obtain information on the shapes of monomeric MX_5 species at low temperatures. Such studies have been reported by Werder *et al.*[13] and by Nunziante-Cesaro *et al.*,[14] where some of the present compounds were isolated in inert-gas matrices and studied by IR spectroscopy. Although these experiments were interpreted assuming the D_{3h} model, we have recently shown on the basis of IR intensity and isotope data[15] that the results are more consistent with the C_{4v} model. We have used the same approach to show that $MoCl_5$ has C_{4v} symmetry in both argon and nitrogen matrices,[16] whereas WCl_5 and WBr_5 have D_{3h}.[17]

Here we report our matrix-isolation spectroscopic studies of the vapour species produced on heating $NbCl_5$, $NbBr_5$, $TaCl_5$, $TaBr_5$, $ReCl_5$, $ReBr_5$ and $OsCl_5$. In addition to IR characterisations, UV/VIS spectra of the monomers are also reported and provisionally assigned.

Experimental

Synthetic Methods.—Samples of $NbCl_5$ (ALFA) and $TaCl_5$ (BDH) were obtained commercially, and freshly sublimed *in vacuo* before use. Some rhenium(v) chloride was obtained commercially (Aldrich), and other samples were made from ReF_6 and BCl_3. Osmium(v) chloride was made from OsF_6 and BCl_3.[18]

Rhenium(v) *bromide.* This was made by the method of Canterford and Waugh.[19] A mixture of ReF_7 and ReF_6, made by heating rhenium powder (5 mmol) in fluorine (40 mmol) at *ca.* 520 K, was condensed at 77 K into a silica ampoule on a vacuum line. An excess of BBr_3 (*ca.* 10 cm^3) was condensed onto it at 77 K, and the mixture allowed to warm slowly. On melting a violent reaction resulted which was moderated by cooling with liquid nitrogen from time to time. When the reaction had subsided a blue-black solution remained, from which volatile materials were removed *in vacuo* at room temperature. These consisted primarily of boron halides, together with some blue (solid) $ReOBr_4$. The residual brown-black powder was transferred to break-seal ampoules in a nitrogen-filled glove-box (H_2O < 10 ppm) (Found: Br, 67.1. Br_5Re requires Br, 68.2%). The X-ray powder diffraction pattern showed the product was poorly crystalline, probably a result of the low temperature of preparation, and the pattern was too poor to index. In view of its thermal instability the product was not sublimed.

Niobium(v) *and tantalum*(v) *bromides.* These materials were made by a modification of the method of Druce and Lappert.[20] Niobium(v) chloride (4 g) was loaded into a glass ampoule in a glove-box, the ampoule attached to a vacuum line, and excess of BBr_3 (*ca.* 15 cm^3) condensed onto it at 77 K, causing the yellow solid to turn dark red. The mixture was refluxed for 72 h, after which the remaining boron halides were distilled away *in vacuo*. The crude $NbBr_5$ was sublimed *in vacuo* into break-seal ampoules. The purified material was a dark purple crystalline solid (Found: Br, 80.9. Br_5Nb requires Br, 81.1%). Use of a smaller excess of BBr_3 or shorter reaction times resulted in a chlorine-containing product.

Tantalum(v) bromide was made similarly as an orange-yellow material (Found: Br, 67.9. Br_5Ta requires Br, 68.8%).

Attempts to prepare $ReBr_5$ from $ReCl_5$ and BBr_3 by this route were unsuccessful.

Spectroscopic Studies.—Sample vaporisation for both the mass spectrometric and matrix-isolation studies was from resistively heated break-seal or tap-ampoules which had previously been flamed in an attempt to remove adsorbed moisture. However, despite this procedure, initial mass spectra often showed the presence of hydrogen chloride and, for some systems, oxide halides were also observed.

Mass spectra were recorded using a modified VG 12-12S quadrupole instrument (mass range 1–2000) interfaced with a data system. The products of vaporisation traversed a line-of-sight path of *ca.* 15 cm into the ionisation region, and ionisation energies were typically *ca.* 24 eV (*ca.* 38×10^{-19} J).

Details of our matrix-isolation IR and UV/VIS apparatus have been described elsewhere.[21] As in previous studies, spectra

Table 1 Observed and calculated IR bands (cm^{-1}) for matrix-isolated rhenium-, niobium- and tantalum-(V) chlorides

	$ReCl_5$		$NbCl_5$		$TaCl_5$	
Matrix	obs.	calc.[a]	obs.	calc.[b]	obs.	calc.[c]
Nitrogen	427.8	427.8	444.1	444.1	426.0	426.0
	—	425.3	435.9	435.9	416.7	416.7
	423.5	423.5	400.4	400.4	371.7	371.7
	418.7	419.1	397.2	397.4	368.5	368.5
	360.2	360.2		397.2		368.3
	357.0	356.9	394.0	394.3	364.5	365.1
	352.9	352.9		394.2		364.4
			391.0	391.0	360.4	360.4
Argon	430.9		456.4 **C**		434.7 —	
	426.8		448.6 **C**		426.3 **Y**	
	422.8		444.5 **B**		423.8 —	
	420.5		443.8 —		420.0 —	
	417.9		438.2 **B**		417.0 **Y**	
	369.7		434.8 **A**		405.0 **X**	
	366.5		432.6 **A**		402.0 **Y**	
	362.4		430.1 **A**		399.0 **X**	
	360.8		427.2 **B**		378.5 —	
	359.2		425.0 **B**		374.4 —	
	357.7		423.0 **B**		368.8 **Y**	
	355.0		405.0 —		364.9 **Y**	
	353.4		402.8 —		361.3 **Y**	
			399.0 —			
			397.5 **B**?			
			396.0 —			
			393.5 —			
			389.8 —			

[a] Assuming a D_{3h} structure. [b] Based on a C_{4v} structure in which basal principal force constants differ by *ca.* 1.5%. [c] Based on a C_{4v} structure in which basal principal force constants differ by *ca.* 2%.

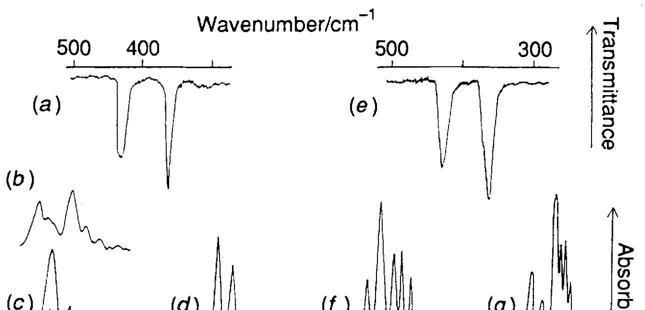

Fig. 1 Infrared spectra obtained from matrix-isolated rhenium(V) chloride: (*a*) low-resolution spectrum in a dinitrogen matrix; (*b*) and (*c*) higher-resolution spectra of the higher-frequency band before and after diffusion, together with computed isotope pattern; (*d*) higher-resolution spectrum of the lower-frequency band, together with computed isotope pattern; (*e*) low-resolution spectrum in an argon matrix; (*f*) and (*g*) higher-resolution spectra of the bands in (*e*)

were run sequentially in order to check sample integrity, and for these present systems it was also possible to obtain mass spectra under identical vaporisation conditions before and after each sequence of matrix experiments. The IR and UV/VIS spectra were obtained in nitrogen or argon (99.999% BOC) matrices, typically in > 1000-fold excess, and during diffusion studies, matrix deposits were slowly warmed from the base temperature of 12 to *ca.* 28 K prior to recooling.

Results and Discussion

As indicated above, all the compounds studied were extremely reactive towards traces of moisture, resulting in the formation of oxide halides. For the niobium and tantalum compounds, these impurities were not a major problem due to their much lower volatility, but for $ReCl_5$ considerable difficulties were experienced in obtaining spectra free from the characteristic absorptions of ReO_3Cl and $ReOCl_4$. These rhenium oxide halides are more volatile than $ReCl_5$, and spectra of the latter free from impurities were only obtained by thoroughly passivating the system with $ReCl_5$ vapour.

Mass spectra were obtained from all the systems studied, with the exception of $OsCl_5$. In all cases except $ReBr_5$, the most prominent ions were the fragments MX_4^+ once oxide halide impurities had been removed. These observations are in general agreement with previous studies on these compounds.[22] In the case of $ReBr_5$, we were unable to detect any $ReBr_4^+$, and the major peaks in the mass spectrum corresponded to the cluster ions $Re_3Br_x^+$, where $x = 4$–9, and $Re_2Br_y^+$, with $y = 3$–6, clearly derived from Re_3Br_9.[23]

Matrix-isolation Studies.—Infrared spectroscopy. The results are summarised in Tables 1 and 2.

$ReCl_5$. Spectra were obtained from samples heated to *ca.* 350 K, and initial deposition in a nitrogen matrix yielded prominent absorptions centred at *ca.* 1040, 425, 390 and 360 cm^{-1}. The features at 1040 and 390 cm^{-1} arise from $ReOCl_4$. The bands at 425 and 360 cm^{-1} are of similar intensity (Fig. 1), and were provisionally assigned to monomeric $ReCl_5$. Corresponding experiments in an argon matrix yielded absorptions at 422 and 362 cm^{-1}.

Under high resolution the absorption at 425 cm^{-1} consists of two prominent components at 429.7 and 424.1 cm^{-1}, and a number of weaker features, whereas the band at 360 cm^{-1} appeared as a well resolved triplet. Diffusion to *ca.* 28 K had little effect on this lower band, but the higher band now showed only one intense component at 427.8 cm^{-1} (Fig. 1). Argon-matrix spectra under high resolution were more complicated; the band at 362 cm^{-1} is interpreted as arising from three triplets, whilst that at 422 cm^{-1} can be regarded as three doublets, arising from split E modes.

$OsCl_5$. Samples of $OsCl_5$ were heated from *ca.* 300 to 500 K, but the only volatile products detected by matrix-isolation IR spectroscopy were $OsOCl_4$ and traces of OsO_4.[24] The apparent lack of a volatile pentachloride is consistent with previous observations,[18] where it was noted that samples undergo thermal decomposition to yield chlorine and an involatile lower chloride.

$NbCl_5$. Vaporisation of niobium pentachloride at *ca.* 310 K gave low-resolution matrix spectra in good agreement with previous work,[13,14] but with negligible oxide chloride impurity. Fig. 2 shows a typical spectrum showing the two monomer features at 444 and 397 cm^{-1}. High-resolution studies show that the feature at 444 cm^{-1} comprises a simple 3:1 doublet with components at 444.1 and 435.9 cm^{-1}, whilst the feature at 397 cm^{-1} contains four components at 400.4, 397.2, 394.0 and 391.0 cm^{-1}. The structure on these absorptions was not affected during mild diffusion, but warming to *ca.* 35 K resulted in a general broadening and loss of intensity, and the growth of a broad absorption at *ca.* 435 cm^{-1} consistent with the formation of $NbCl_5$ aggregates.[14]

Initial spectra in argon matrices often showed features very similar to those observed in nitrogen, *viz.* two absorptions at *ca.* 444 and 397 cm^{-1},[13,14] and under higher resolution the band at 444 cm^{-1} showed a poorly resolved doublet. However, spectra obtained from samples at a later stage in deposition, or from samples which had been repeatedly resublimed, showed several absorptions over the range 470–380 cm^{-1}, which yielded at least fifteen sharp components under high resolution.

Fig. 2(*e*) shows a typical high-resolution argon-matrix spectrum obtained from a sample of $NbCl_5$ which had been

Table 2 Observed and calculated IR bands (cm^{-1}) for matrix-isolated niobium- and tantalum-(v) bromides

$NbBr_5$			$TaBr_5$			
Matrix			Matrix			
Ar	N_2	Calc.*	Ar	N_2	Calc.*	Assignment
	318.8	318.8		282.1	282.1	A_1 M-^{79}Br
	317.1	317.1		280.0	280.0	A_1 M-^{81}Br
	290.0			250.0		E M-Br
332.6w			289.6w			
316.2s			287.3w			
307.7w			278.8m			
298.2s			275.9s			
290.5s			269.9m			
242.9w			268.0 (sh)			
			255.4s			
			247.4s			

* Calculated for a diatomic M-Br unit with stretching constants F_{Nb-Br} = 2.5634 and F_{Ta-Br} = 1.9987 mdyn Å^{-1} (dyn = 10^{-5} N).

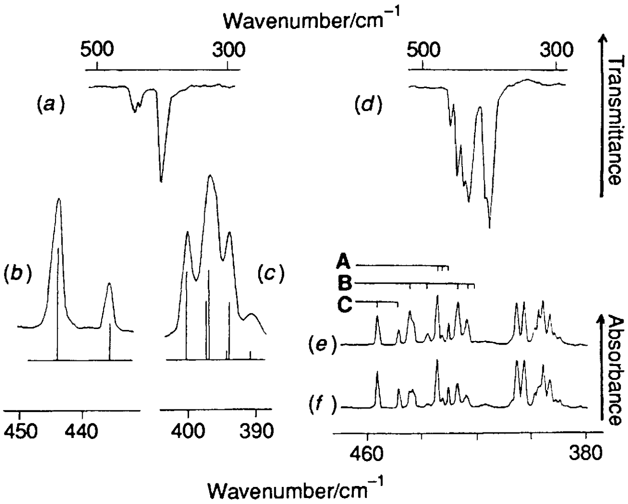

Fig. 2 Infrared spectra obtained from matrix-isolated niobium(v) chloride: (*a*) low-resolution spectrum in a dinitrogen matrix; (*b*) and (*c*) higher-resolution spectra of the bands in (*a*), together with computed isotope patterns; (*d*) low-resolution spectrum in an argon matrix; (*e*) and (*f*) higher-resolution spectra of the bands in (*d*) before and after diffusion

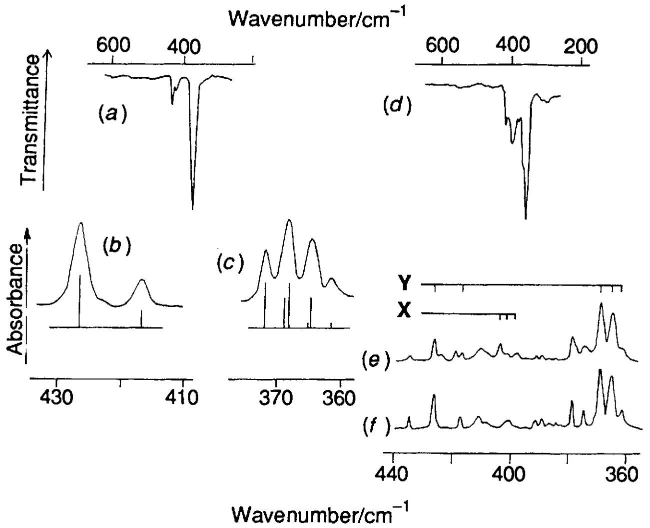

Fig. 3 Infrared spectra obtained from matrix-isolated tantalum(v) chloride. Details as in Fig. 2

resublimed immediately prior to deposition. Mild diffusion to *ca.* 28 K permitted the identification of at least two distinct groups of absorptions. Species **B** is characterised by a group of bands which decrease on diffusion, and the components comprising **A** and **C** (Table 1) could be distinguished from separate experiments.

$TaCl_5$. Infrared spectra obtained from the vaporisation of $TaCl_5$ at *ca.* 320 K were qualitatively almost identical to those obtained for $NbCl_5$. Thus in nitrogen under low resolution two bands were observed at 426 and 368 cm^{-1}, which on closer examination showed doublet and quartet patterns respectively (Fig. 3). In argon, absorptions extended from *ca.* 440 to 360 cm^{-1} [Fig. 3(*e*)] and although diffusion studies were less conclusive they indicated parallel intensity behaviour for the groups of absorptions identified as **X** and **Y**.

$ReBr_5$. Samples of $ReBr_5$ sublimed at *ca.* 460 K produce IR spectra consisting of two relatively broad (5 cm^{-1}) absorptions. In nitrogen matrices these were centred at 289.8 and 246.4 cm^{-1}, and in argon at 289.0 and 246.8 cm^{-1}. No significant spectral changes were observed on diffusion.

$NbBr_5$. Vaporisation of $NbBr_5$ at *ca.* 290 K gave two bands, at 318 and 290 cm^{-1}, in a nitrogen matrix (Fig. 4). Under high resolution the higher-frequency absorption is a doublet, with components at 318.8 and 317.1 cm^{-1}. In argon, the spectrum consisted of several features, notably at 316 and 298/290 cm^{-1}, and diffusion studies indicated the presence of more than one entity.

$TaBr_5$. A typical nitrogen-matrix spectrum obtained from the vaporisation of $TaBr_5$ at *ca.* 370 K is shown in Fig. 4. Under high resolution the less-intense feature at 281 cm^{-1} appears as a partially resolved doublet (282.1/280.0 cm^{-1}), while the intense band at 250 cm^{-1} reveals a partially resolved shoulder at 253 cm^{-1}. In argon the spectrum showed a cluster of bands similar to those observed for $NbBr_5$, with prominent absorptions at 275.9 and 255.4/247.4 cm^{-1}.

Vibrational analysis. Normal coordinate analyses for D_{3h} and C_{4v} MX_5 species are well documented, and a unified approach to establishing the shapes of MCl_5 species in low-temperature matrices which uses both IR selection rules and chlorine isotope patterns has recently been described.[15] Briefly, the D_{3h} trigonal bipyramid structure is expected to show two prominent M-Cl stretching modes (A_2'' + E') with an approximate intensity ratio 2:3. Under high resolution these two absorptions should show characteristic triplet and quartet patterns respectively arising from the two naturally occurring chlorine isotopes. The C_{4v} square pyramid should also show two prominent IR stretches (A_1 axial + E) but the expected intensity ratio is now *ca.* 1:4, and under high resolution the chlorine isotopes should yield a 3:1 doublet and a 9:6:1 triplet respectively. This analysis is in principle transferable directly to the analogous pentabromides, and as the natural abundance ratio

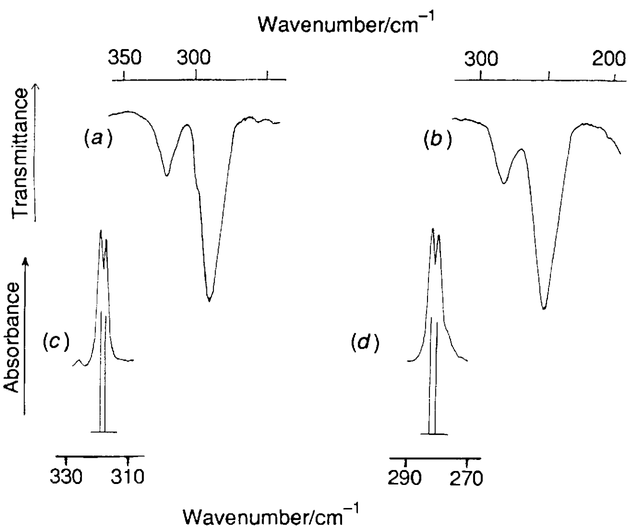

Fig. 4 Infrared spectra obtained from niobium(v) and tantalum(v) bromides isolated in dinitrogen matrices: (*a*) and (*b*) low-resolution spectra of $NbBr_5$ and $TaBr_5$; (*c*) and (*d*) higher-resolution spectra of the higher-frequency bands in (*a*) and (*b*), together with computed isotope patterns

of $^{79}Br/^{81}Br$ isotopes is close to 1:1 the resulting patterns should correspondingly appear as a 1:1 doublet and a 1:2:1 triplet.

Rhenium pentachloride and pentabromide. The nitrogen- and argon-matrix spectra obtained from ReX_5 under low resolution all show two prominent bands of similar intensity, suggesting the isolation of monomeric species with D_{3h} symmetry, and high-resolution and diffusion experiments confirmed this assignment. Thus for $ReCl_5$ in nitrogen we assign the lower-frequency band at 360 cm^{-1} as the A_2'' stretch, since it shows a well resolved 9:6:1 triplet, and the band at *ca.* 427 cm^{-1} as the E$'$ mode. Under higher resolution *before* diffusion this latter mode consists of two prominent features at 429.7 and 424.1 cm^{-1}, but on gentle warming these coalesce to a single intense component at 427.8 cm^{-1}, together with weaker features. The resulting pattern now resembles the isotope structure expected for a planar MCl_3 unit,[25] and the computed spectrum summarises the results of our spectral simulation based on the D_{3h} model. Argon-matrix spectra are consistent with the trapping of a D_{3h} monomer on three sites (Table 1).

The nitrogen-matrix spectra obtained from $ReBr_5$ under low resolution were qualitatively very similar to those from $ReCl_5$, and we initially believed that they could satisfactorily be assigned to D_{3h} $ReBr_5$. However, the mass spectral data indicated that, under identical vaporisation conditions, Re_3Br_9 was the vaporising species, and that there was no evidence for a simple monomer. Electron diffraction studies indicate that Re_3Br_9 has D_{3h} symmetry,[26] and for this structure the vibrations of the six terminal Re–Br bonds transform as $A_1' + A_2'' + E' + E''$. We assign the observed vibrations to the IR-active $A_2'' + E'$ modes.

Niobium and tantalum halides: nitrogen-matrix IR spectra. The spectra obtained for NbX_5 and TaX_5 under low resolution all show two absorptions with the approximate intensity ratio 1:4, indicative of a C_{4v} structure. The intense component is the equatorial E stretch, and the weaker, higher-frequency band is the axial A_1. These assignments are confirmed by the characteristic doublet structure present in the high-resolution scans of the A_1 mode. However, the E modes do not show the simple triplet patterns anticipated for C_{4v} symmetry. In particular, the chlorides should exhibit 9:6:1 patterns, and the bromides 1:2:1 patterns. Instead, the structure observed for both chlorides is a rather asymmetric quartet, whilst the bromides show little or no structure. This latter observation is not unexpected, but it is important to understand the origin of the quartets for the chlorides. We believe that in these nitrogen matrices the unsymmetrical nature of the trapping site causes a small splitting of the E mode, such that the two components have slightly different frequencies, but remain orthogonal. Since each component is still effectively a vibrating MX_2 unit, two closely spaced isotope patterns will result. The observed spectrum could then arise if the splittings of the degeneracies were comparable with the isotope shifts in the 9:6:1 triplets. This interpretation is consistent with several other studies[21,24,27] which show similar degenerate mode splittings in nitrogen matrices.

The line diagrams (Figs. 2–4) summarise the results of spectral simulations for the C_{4v} model in which the stretching modes are decoupled from the bends, and the bond-dipole derivatives for axial and equatorial bonds are taken to be equal. Our model assumes that the splitting of the E mode arises from slightly different force constants rather than a distortion of bond angles, and the calculated frequencies are summarised in Table 1.

Argon-matrix spectra. In contrast to the nitrogen-matrix spectra, our argon results for $NbCl_5$ and $TaCl_5$ showed some variation, depending upon deposition conditions. The initial spectra were qualitatively similar to those obtained in nitrogen, and those reported previously.[13,14] However, samples which had been purified by repeated sublimation yielded spectra consisting of a large number of sharp features over a range of *ca.* 90 cm^{-1}. For purified $NbCl_5$ and $TaCl_5$, controlled diffusion produced significant intensity changes in several of the sharp components. No features appeared in the bridging region during such studies, and therefore halide-bridged dimers are not responsible for these changes.

For $NbCl_5$ (Fig. 2) the group of bands labelled **A** are indicative of a D_{3h} monomer, whilst a possible C_{4v} isomer is indicated by the doublet and triplet features **B**. We tentatively assign **C** to a lower-symmetry structure (C_{2v} or C_s) which also has a single Nb–Cl unit, as revealed by a second 3:1 doublet. The high-resolution spectra observed for $TaCl_5$ in argon are also complex (Fig. 3): the set of bands labelled **X** suggests a D_{3h} isomer, whilst a square-pyramidal moiety is indicated by **Y**.

The traditional explanation for the multiplicity of bands commonly found in argon matrices is the concept of 'site effects', where molecules of the *same basic structure* suffer small differential matrix shifts. Until quite recently, it could confidently be stated that 'There are no convincing cases in which molecular symmetry differs in gas and matrix phases',[28] and matrix experiments have been used routinely as an indication of vapour-phase molecular structure. Our results for $ReCl_5$ are consistent with this view. For the niobium and tantalum halides, however, the matrix may play a more significant role. A change in the equilibrium geometry of a molecule as a result of dinitrogen co-ordination is perhaps not unexpected,[29] but examples of specific co-ordination by argon seem less likely, although recent studies dispute the above premise,[30–32] most notably the suggestion of adduct formation between $ThCl_4$ and argon or krypton, in which the $ThCl_4$ unit is significantly distorted from its (presumed) vapour-phase equilibrium structure.[32]

We believe that the d^0 pentahalides may similarly be susceptible to changes in geometry resulting from interaction with the matrix environment. In nitrogen we propose co-ordination at the sixth site of an octahedron, but the behaviour in argon matrices is less clear. Initial deposition freezes out a mixture containing D_{3h}, C_{4v} and at least one other low-symmetry isomer. Controlled diffusion results in further reaction, but at no stage was the spectrum sufficiently simple for it to be assignable to a single entity.

UV/VIS spectroscopy. Spectra were obtained over the range 900–190 nm (*ca.* 11 000–52 000 cm^{-1}) for all systems except $ReBr_5$ and $OsCl_5$. The major bands are listed in Table 3, and survey spectra are shown in Fig. 5. The niobium and tantalum compounds have C_{4v} geometries in nitrogen matrices (above),

Table 3 Ultraviolet–visible spectral data (E_{max}/cm^{-1}) for niobium-, tantalum- and rhenium-(V) halides in nitrogen matrices

$NbCl_5$	$TaCl_5$	$NbBr_5$	$TaBr_5$	$ReCl_5$
31 250	37 760	25 220	30 960	22 650
35 330	41 320	27 850	34 550	26 150
39 500	45 450	31 990	38 700	29 600
42 050	50 000 (sh)	37 900	41 800 (sh)	36 000
43 500		44 200	45 250	43 500
48 200				50 200

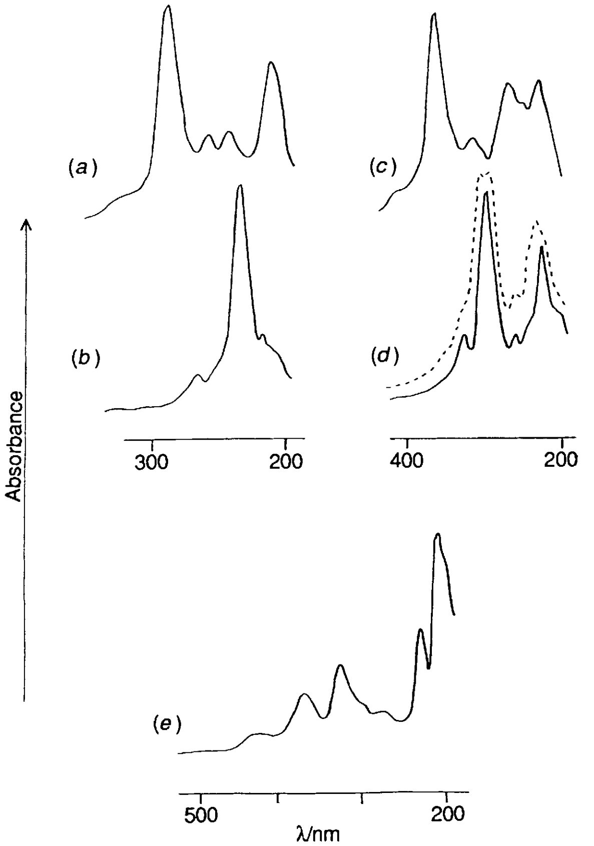

Fig. 5 Ultraviolet–visible spectra of matrix-isolated pentahalides: (*a*) $NbCl_5$ in N_2; (*b*) $TaCl_5$ in N_2; (*c*) $NbBr_5$ in N_2; (*d*) $TaBr_5$ in N_2 (——) and Ar (- - -); (*e*) $ReCl_5$ in N_2

and for these d^0 metal centres all transitions must be charge transfer (c.t.) Cl(Br)→Nb(Ta) in type. Consideration of the spectra of the two chlorides shows them to be very similar in profile, with the corresponding absorptions for $TaCl_5$ *ca.* 6000 cm^{-1} to higher energy than observed for $NbCl_5$. Similar comparisons can be drawn between $NbBr_5$ and $TaBr_5$. Comparison of the spectra of $NbCl_5$ with those of $NbBr_5$, and $TaCl_5$ with $TaBr_5$, shows that the lowest charge-transfer transition shifts *ca.* 6000 cm^{-1} to low energy on replacing chlorine with bromine, but detailed examination shows that the patterns for the higher energy bands correlate less well. The bromides have broader features, probably reflecting the greater spin–orbit coupling constant of bromine which would be expected to lead to band broadening or splittings.[33]

In C_{4v} geometry the metal d-orbital ordering is likely to be e (d_{xz}, d_{yz}) < b_2 (d_{xy}) < a_1 (d_{z^2}) < b_1 ($d_{x^2-y^2}$), whilst the halogen π orbitals transform as $A_1 + A_2 + B_1 + B_2 + 2E$, and the σ set transform as $2A_1 + B_1 + E$. From this it is clear that many more charge-transfer transitions are predicted than are evident as resolved bands in the spectra, and hence detailed assignments are impractical on the basis of available evidence. However the optical electronegativity model[34] can be used to predict the lowest-energy c.t. band for each compound. For d^0 metal centres the lowest-energy transition is $E_{max}\,(10^3\ cm^{-1}) = 30\,000(\chi^{opt}\,X - \chi^{opt}\,M)$ where χ^{opt} Cl and χ^{opt} Br have the usual values for the π orbitals of 3.0 and 2.8.[35] Taking E_{max} as the lowest-energy feature in the spectrum of $NbCl_5$ (31 250 cm^{-1}) gave χ^{opt} Nb^V of 1.95. Using this value one can predict the lowest-energy band in the spectrum of $NbBr_5$ as 25 500 cm^{-1}, compared with the observed value of 25 220 cm^{-1}. Similarly one can calculate χ^{opt} of 1.75 for Ta^V from the chloride data, and predict the lowest-energy band for $TaBr_5$ as 31 500 cm^{-1} compared with the experimental value of 30 960 cm^{-1}. The energies of these charge-transfer bands also correlate well with the data reported[36] for the corresponding octahedral $[MX_6]^-$ (M = Nb or Ta, X = Cl or Br), which is expected since previous studies have shown little difference between the optical electronegativities of the metals in five- and six-co-ordinate environments.

Some spectra were also obtained in argon matrices, for which the IR data indicate a mixture of geometries were present, and one example is shown in Fig. 5. The spectrum is slightly different and the bands are broader than in the nitrogen matrix. One would not expect great differences between the charge-transfer spectra of an MX_5 species in C_{4v} and D_{3h} geometries, but these differences support the conclusions from the IR studies.

The assignment of the spectrum of rhenium(V) chloride is less straightforward since the metal has a d^2 configuration, and hence both d–d and c.t. bands are expected. For Re^V in a trigonal-bipyramidal field the d-electron configuration is expected to be $e''^2 < e'^0 < a_1{}^0$, and in the strong-field model, spin-allowed transitions from e″ to e′ and to a_1 are expected. The e″ − e′ separation is likely to be relatively small even in the 5d series, and this transition is expected in the near-IR region outside the range of the spectrometer. The e″ ⟶ a_1 transition is provisionally assigned as the feature at 22 650 cm^{-1}, with the higher-energy features as c.t. bands. In the case of $ReCl_5$, the lowest-energy charge-transfer transition is predicted as $E_{max} = 30\,000(\chi^{opt}\,Cl - \chi^{opt}\,Re^V) + \frac{5D}{3}$ where $\frac{5D}{3}$ corresponds to the change in spin-pairing energy from $S = 1$ to $S = \frac{1}{2}$ and D is the Racah parameter. D is not known for most 5d ions, but if we adopt the value of 2500 cm^{-1} from ReF_6[37] we obtain χ^{opt} Re^V as 2.25. The value is not corrected for spin–orbit effects, but even so seems reasonable.

Conclusion

For $ReCl_5$, where argon and nitrogen matrices yield similar spectra, we believe that the D_{3h} structure derived from IR isotope patterns is a firm indication of the vapour-phase geometry, and that the corresponding electronic spectra also provide relevant molecular information.

However, in the case of the four d^0 species, the matrix environment plays a significant role, and no firm conclusions can be drawn regarding vapour-phase properties. Nitrogen matrices produce only the C_{4v} structure, but our argon-matrix spectra are capable of at least two interpretations. First, it is possible that our conditions of rapid freezing result in the trapping of a mixture of conformers. However, in view of the earlier data on $ThCl_4$, it is also possible that specific adducts between MX_5 and argon are formed, and it is surely significant that niobium and tantalum pentahalides form very stable Lewis adducts. The lack of any ligand-field stabilisation energy for these d^0 species may also be important.

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