Spectroscopic Studies on Matrix Isolated Tungsten Chlorides and Bromides

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Tungsten pentachloride has been heated in high vacuum, and the vapour species isolated in inert matrices at *ca.* 12 K. Subsequent i.r. spectra showed intense features at 410 and 365 cm^{-1} which are assigned as the A_2'' and E' stretching modes respectively of monomeric D_{3h} WCl_5. Corresponding studies on the hexachloride showed that monomeric WCl_6 could similarly be isolated, and for this species, the u.v.–visible spectrum was also obtained and analysed in detail. The vaporisation of tungsten bromide samples of typical stoicheiometry $WBr_{5.3}$ yielded a new spectroscopic feature in the matrix i.r. spectrum at *ca.* 305 cm^{-1} which is assigned to molecular WBr_6. At higher temperatures, the vaporisation of the solid pentabromide resulted in bands at 280 and 245 cm^{-1} which are assigned as the A_2'' and E' stretching modes in D_{3h} WBr_5.

Research into the chemistry of the hexa- and penta-halides of the transition metals has largely been confined to the fluorides. For these compounds, extensive structural and spectroscopic studies have been carried out, and they have attracted several detailed reviews.[1–4] In contrast, significantly less information is available on the corresponding chlorides, and apart from a few notable exceptions, work in this area is largely confined to the solid phase. Thus for solid tungsten hexachloride, two polymorphs are known,[5,6] and Raman,[7] i.r.,[8] and u.v.–visible[9–11] spectra have been analysed; however, in the vapour phase, spectroscopic data are limited to one u.v.–visible study,[12] a single report of the T_{1u} stretch in the i.r.,[13] and an unpublished Raman study.[14] The crystal structure of tungsten pentachloride shows the presence of dimeric units,[15] but the only vapour phase characterisation appears to be a mass spectrometric study[16] and a u.v.–visible study[12] in which it is concluded that the vapour contains both monomer and dimer species.

The corresponding tungsten bromides are less well characterised. The traditional route to the hexabromide from the reaction between $W(CO)_6$ and Br_2 yields a stoicheiometric product which is stable at 273 K,[17] but which evolves Br_2 on warming *in vacuo* to room temperature. A recent crystal structure determination[18] has established that the solid contains octahedral WBr_6 units, but attempts to identify this molecule in the vapour phase by mass spectrometry revealed only decomposition products,[19] and it was concluded that WBr_6 did not exist in the vapour phase. The pentabromide, however, appears to be stable in the vapour, and to exist primarily as a monomer,[19] although no spectroscopic or structural data have been reported.

The analogous molybdenum halides are, in many respects, even more elusive. No claims appear to have been made for either $MoBr_5$ or $MoBr_6$, and although a preliminary report has indicated[20] that molybdenum hexachloride can be prepared from the reaction between thionyl chloride and molybdic acid, no spectroscopic data to support this formulation have been forthcoming. The pentachloride is a commercially available material, but there remains an unresolved controversy regarding the shape of the vapour species. Raman studies on this system by Beattie and Ozin[21] indicated that the vapour consists primarily of D_{3h} monomers, whereas a subsequent electron diffraction study by Brunvoll *et al.*[22] concluded that both C_{4v} and D_{3h} monomers were present, together with a smaller proportion of D_{2d} dimer.

As part of our continuing investigation of transition metal halides and oxide halides,[23–25] this paper describes our matrix isolation studies on the vapour species present above heated samples of tungsten(V) and tungsten(VI) chlorides and bromides. Our principal aims were first to characterise the vapour species using i.r. spectroscopy, and, in the case of WCl_6, subsequently to obtain u.v.–visible data of sufficient quality to permit detailed assignment.

We also hoped that these experiments would provide some support for at least one of the interpretations currently offered regarding $MoCl_5$, since it is well known that the molecular complexes of molybdenum and tungsten are frequently isostructural.

Experimental

Tungsten(VI) chloride was prepared from $W(CO)_6$ and liquid Cl_2 at *ca.* 200 K, the reaction being completed by warming the black product to *ca.* 320 K in a chlorine atmosphere (Found: Cl, 53.5. Calc. for WCl_6: Cl, 53.7%). Samples of tungsten(V) chloride were prepared from the hexachloride by reaction with tetrachloroethylene in the presence of strong light, in accord with the conditions described by Brown and McCann[26] (Found: Cl, 49.7. Calc. for WCl_5: Cl, 49.1%). Both materials were purified by vacuum sublimation prior to use.

Samples of blue-black tungsten(VI) bromide were prepared by the reaction between $W(CO)_6$ and Br_2, following the method of Crouch *et al.*[17] However, this material is known to evolve bromine at room temperature under modest vacuum to yield a material with stoicheiometry *ca.* $WBr_{5.8}$. After prolonged pumping under high vacuum, our samples gave a typical composition $WBr_{5.3}$ (Found: Br, 69.7. Calc. for WBr_6: 72.3. Calc. for $WBr_{5.3}$: 69.7%). On heating this material *in vacuo* to *ca.* 410 K, stoicheiometric WBr_5 can be produced.[17] Samples of our '$WBr_{5.3}$' treated in this way analysed to give: Br, 68.4 (Calc. for WBr_5: 68.5%).

Details of our matrix isolation equipment and spectroscopic instrumentation are described elsewhere.[23] For this present work, all sample manipulation was carried out in glass vacuum lines fitted with greaseless joints and taps [poly(tetrafluoroethylene), J. T. Young]. During deposition, samples were heated in Pyrex tap ampoules within the temperature range 300—600 K, and high purity nitrogen and argon (BOC, 99.999%) were used as matrix gases.

Results and Discussion

Tungsten Hexachloride.—The i.r. and Raman spectra of monomeric WCl_6 have been reported previously,[27,28] and in particular, the single i.r.-active stretching mode lies at 365 cm^{-1} in CCl_4 solution[27] and at *ca.* 387 cm^{-1} in the vapour phase.[13] The main purpose in carrying out matrix i.r. studies on this

Table 1. Infrared stretching frequencies (cm^{-1}) observed for monomeric tungsten-(V) and -(VI) chlorides and bromides

Assignments	This work[a]	Previous work
WCl_6 $\nu(T_{1u})$	367[b]	365[c] 387[d]
WBr_6 $\nu(T_{1u})$	305[e]	
WCl_5 $\nu(A_2'')$	410[b]	
$\nu(E')$	365[b]	
WBr_5 $\nu(A_2'')$	280[e]	
$\nu(E')$	245[e]	

[a] Centre of complex or broad absorption. Frequency accuracy ±2 cm^{-1}. [b] Nitrogen matrix. [c] Ref. 27. [d] Ref. 13. [e] Argon matrix.

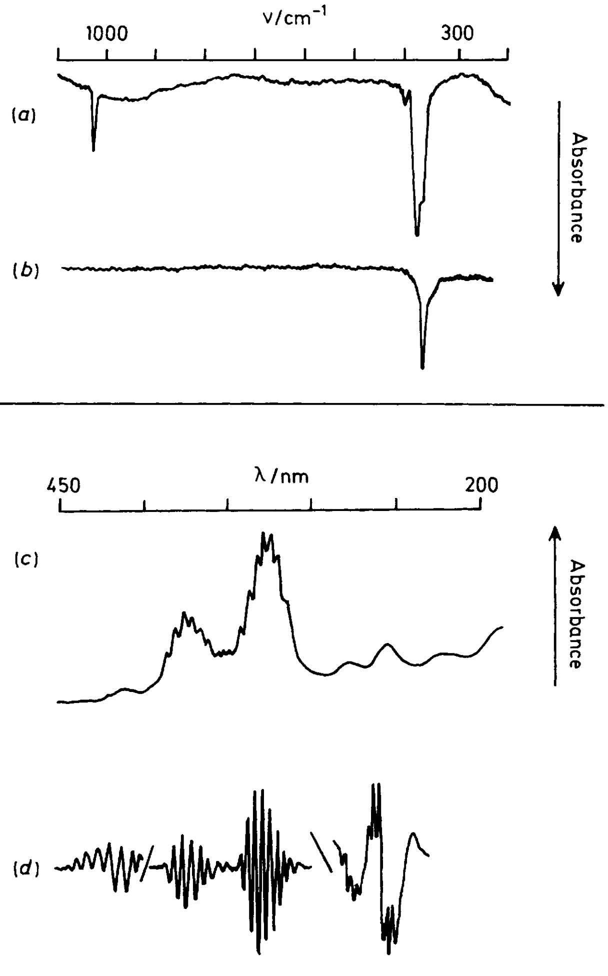

Figure 1. Nitrogen matrix i.r. and u.v.–visible spectra obtained from tungsten(VI) chloride. (*a*) I.r. spectrum after initial stages of deposition, vaporisation temperature *ca.* 340 K; (*b*) as (*a*), but after removal of traces of water from the spray-on system; (*c*) u.v.–visible spectrum of WCl_6; (*d*) as (*c*), but with derivative recording

Table 2. U.v.–visible absorption bands (cm^{-1}) for WCl_6

Ref. 9 (CCl_4 solution)	Ref. 10 (solid)	Ref. 11 (solid)	Ref. 12 (vapour)	This work* (N_2 matrix)	Assignments
	16 000				
		20 300 (sh)			
22 400 (sh)		22 400 (sh)	23 200	24 350 (300)	$\pi t_{1g} \rightarrow W\ t_{2g}$
26 400	25 000	25 800	27 000	26 700 (375)	$\pi t_{1u} \rightarrow W\ t_{2g}$
29 900	34 000	34 000	30 800	30 570 (375)	$\pi t_{2u} \rightarrow W\ t_{2g}$
		37 400 (sh)		36 350 (385)	$\pi t_{2g} \rightarrow W\ t_{2g}$
			39 000	39 835 (385)	$\sigma t_{1u} \rightarrow W\ t_{2g}$
		44 000		45 800	$\sigma e_g \rightarrow W\ t_{2g}$

* Vibrational spacings in parentheses (±25 cm^{-1}).

system was to establish appropriate deposition conditions for subsequent u.v.–visible studies, and to check sample purity.

During the initial stages of a typical nitrogen matrix experiment, three peaks were routinely observed to grow concurrently. These were located at *ca.* 1 030 and 380 and a shoulder at 367 cm^{-1}. By comparison with previous studies,[23] the features at 1 030 and 380 cm^{-1} are due to $WOCl_4$, whilst the shoulder is assigned to WCl_6. However, as deposition continued, only this latter band continued to increase in intensity. Figure 1(*a*) and (*b*) show typical i.r. spectra recorded at different stages of deposition, and Table 1 compares the data observed here with earlier experimental results.

The presence of $WOCl_4$ in our initial spectra is almost certainly due to hydrolysis occurring in those parts of the glass spray-on system which could not be flamed prior to deposition. However, it was possible to minimise the presence of this impurity either by passing WCl_6 through the inlet system prior to cool-down, or by blocking the line-of-sight path to the cold central window during the early stages of deposition.

The results of previous u.v.–visible[9–12] studies on WCl_6 are summarised in Table 2. When suitable allowance is made for the different media employed (solid, CCl_4 solution, vapour), the spectra are in general agreement, with the single exception of the data reported by Eichler and Seifert.[10] This latter study reports one feature which is so different from the other spectra, that one must conclude that a significant proportion of additional material was present in their samples: perhaps an oxo-halide, or possibly a lower binary chloride. However, in none of these studies was extensive vibrational fine structure observed which might support a spectral assignment.

Figure 1(*c*) shows the u.v.–visible spectrum obtained from WCl_6 isolated in a nitrogen matrix. Five of the six absorptions show vibrational progressions, and these are displayed more clearly in Figure 1(*d*) using derivative recording. The vibrational progressions for each band are included in Table 2. Four of these electronic absorptions appear to involve the same vibrational fundamental in the excited state (*ca.* 380 cm^{-1}) and the most probable mode seems to be the totally symmetric stretch, which occurs at 437 cm^{-1} in the ground state.[28] The absorption at 24 350 cm^{-1}, however, shows a vibrational progression of only *ca.* 300 cm^{-1}. This implies a different excited state fundamental, and the most likely candidate appears to be either the T_{1u} or E_g stretches, which lie at 373 and 331 cm^{-1} respectively in the ground state.[28]

The general assignment of charge-transfer spectra in octahedral MX_6 species has been studied in considerable detail.[9,29] The chlorine π orbitals transform as $t_{1g} + t_{1u} + t_{2u} + t_{2g}$, and the σ set as $t_{1u} + e_g + a_{1g}$. The two intense features at *ca.* 26 700 and 30 570 cm^{-1} are readily assigned to the allowed πt_{1u} and πt_{2u} to W t_{2g} transitions respectively, whilst the weak, low-energy feature at 24 350 cm^{-1} is assigned to the parity-forbidden πt_{1g} to W t_{2g} transition, which gains intensity as a consequence

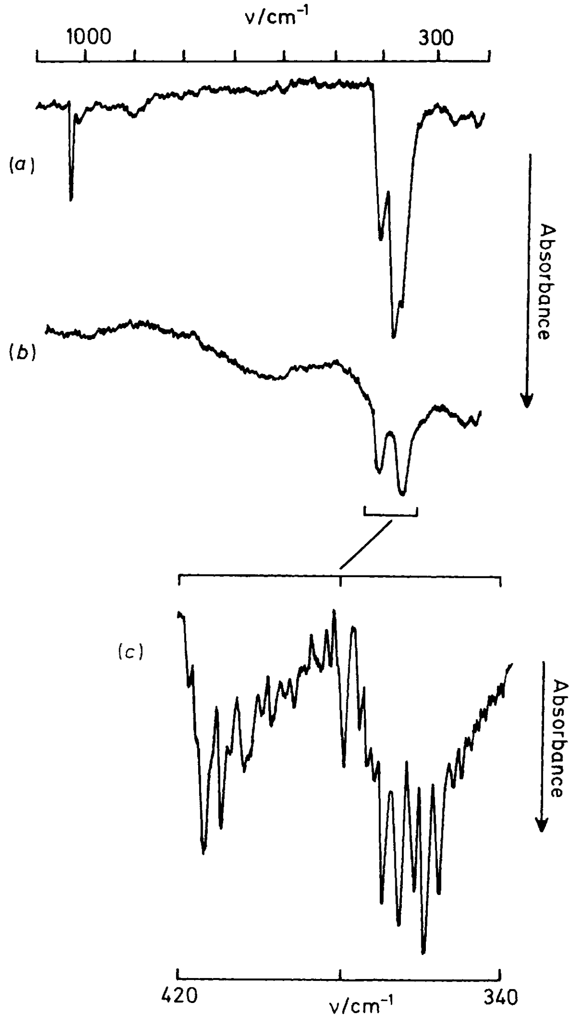

Figure 2. Nitrogen matrix i.r. spectra obtained from tungsten(V) chloride. (*a*) During the initial stages of deposition, vaporisation temperature *ca.* 500 K; (*b*) at a later stage: difference between successive spectra; (*c*) as (*b*), but with a resolution of *ca.* 0.5 cm^{-1}

of vibronic coupling. The remaining πt_{2g} to W t_{2g} transition is therefore identified as the feature at 36 350 cm^{-1}.

In addition, our spectra show two weak high-energy features at 39 835 and 45 800 cm^{-1}. These are tentatively assigned as σt_{1u} and σe_g to W t_{2g} respectively. The alternative assignment of π_u to W e_g for the 45 800 cm^{-1} band was rejected on two grounds. First, it is expected to be relatively intense, and secondly, it would imply a separation t_{2g}–e_g (*i.e.* 10*Dq*) for tungsten of only *ca.* 20 000 cm^{-1}. Even though Cl is a weak field ligand, this value seems rather small compared with the estimates of 28 000 and 40 000 cm^{-1} which have been suggested [3,30] for this parameter in ReF_6 and MoF_6 respectively.

Tungsten Pentachloride.—As indicated previously, there appear to be no published structural or i.r. spectroscopic data on vapour phase tungsten pentachloride, although mass spectrometric studies have shown that monomeric WCl_5 is an important component.[16] Figure 2(*a*) shows part of a typical nitrogen matrix i.r. spectrum obtained at an early stage in the vaporisation of tungsten pentachloride. Four relatively intense absorptions are observed at *ca.* 1 030, 410, 380, and 365 cm^{-1}. By comparison with earlier studies, the bands at 1 030 and 380 cm^{-1} are again identified as fundamentals of $WOCl_4$, formed as the result of hydrolysis. However, as deposition proceeds, these absorptions no longer increase in intensity, and the spectrum becomes dominated by the two features at 410 and 365 cm^{-1}. A typical difference spectrum recorded at this later stage in the experiment is shown in Figure 2(*b*).

The presence of essentially only two i.r.-active W–Cl stretching absorptions indicates that there is unlikely to be more than one conformer trapped in the matrix. In addition, the intensity ratio of the 410 and 365 cm^{-1} bands is close to 2:3, and it may be shown,[31] on the basis of a simple bond dipole approach, that these features correspond closely to the expected relative intensities of the A_2'' and E' modes of the D_{3h} model. For the C_{4v} structure, three i.r.-active W–Cl stretching modes are predicted, with the two most prominent bands showing an intensity ratio of *ca.* 4:1.

On the basis of the low-resolution spectrum, we therefore conclude that monomeric WCl_5 has D_{3h} symmetry when isolated in a low-temperature nitrogen matrix, and assign the A_2'' and E' stretching mode at 410 and 365 cm^{-1} respectively.

Under high resolution, both these features gave complex patterns, as might be anticipated from the plethora of isotopic species present in this system, and Figure 2(*c*) shows a typical spectrum obtained at a resolution of *ca.* 0.5 cm^{-1}. In principle, the isotope structure present on these features provides a means of confirming our spectral assignments in detail. However, the positions of the remaining (i.r.-inactive) stretching modes in WCl_5 are as yet unknown. As a result, there are insufficient potential constants available for a rigorous spectral simulation of these patterns to be worthwhile. Nevertheless, it is evident that the major components of both absorptions show splittings of *ca.* 3—5 cm^{-1}, which is consistent with chlorine isotope effects observed elsewhere.[25,32]

Tungsten Bromides.—Until very recently, the existence of a stable hexabromide of tungsten was in some doubt. Attempts to synthesise this compound reportedly [17] yielded a non-stoicheiometric material at room temperature with the approximate composition $WBr_{5.8}$. On heating to *ca.* 410 K, this material evolved bromine, and the residual solid was found to be tungsten pentabromide.[17] However, Willing and Muller [18] have shown that if the reaction product is kept cold, then its *X*-ray structure corresponds to the hexabromide, and that the WBr_6 units are regular octahedra.

Mass spectrometric studies on both the 'hexabromide' and the pentabromide [19] indicate that monomeric WBr_5 is the prominent vapour species, but no structural or spectroscopic characterisation has been reported.

As indicated earlier, our syntheses of 'tungsten hexabromide' resulted in a dark material with approximate composition $WBr_{5.3}$ which appeared to be stable under high vacuum conditions. Matrix isolation i.r. studies were carried out over the temperature range 500—600 K, and although some bromine was evolved, these experiments gave reproducible i.r. absorptions in the W–Br stretching region.

Figure 3(*a*) shows part of an argon matrix i.r. spectrum obtained during the initial stages of deposition. Five bands may be identified, at *ca.* 1 020, 305, 280, 260, and 245 cm^{-1}. By comparison with previous work,[23] the weak sharp absorptions at 1 020 and 260 cm^{-1} are due to $WOBr_4$, but the low-frequency region also contains three additional features at 305, 280, and 245 cm^{-1}, which have not previously been reported. Figure 3(*b*) shows the spectrum recorded at a later stage in the deposition. All the bands have increased in intensity, but those at 280 and 245 cm^{-1} have now become considerably more prominent.

Figure 3(*c*) shows a typical difference spectrum obtained in the final stages of the experiment where the sample temperature had reached *ca.* 580 K. The $WOBr_4$ features, and the band at 305 cm^{-1} are effectively absent in this spectrum, as they are no

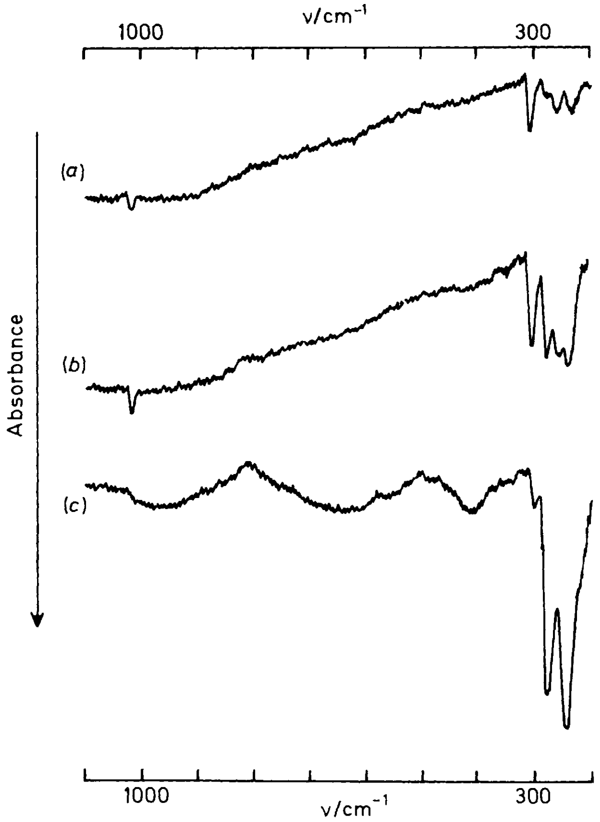

Figure 3. Argon matrix i.r. spectra obtained from tungsten bromide samples: (*a*) during the initial stages of deposition, vaporisation temperature *ca.* 470 K, sample stoicheiometry $WBr_{5.3}$; (*b*) after further deposition at *ca.* 520 K; (*c*) in the final stages of deposition, vaporisation temperature *ca.* 580 K, difference between successive spectra

longer growing, but the absorptions at 280 and 245 cm^{-1} have continued to increase.

On the basis of these, and related experiments, we therefore conclude that two distinct species are isolated in the initial stages of the vaporisation of $WBr_{5.3}$. These are $WOBr_4$ and a second compound which shows a single W–Br stretching absorption at 305 cm^{-1}. The presence of $WOBr_4$ in this system almost certainly arises from hydrolysis, in a similar way to the formation of $WOCl_4$ in the chloride systems, but the band at 305 cm^{-1}, which occurs with $WOBr_4$ in the initial stages of deposition is tentatively assigned as the T_{1u} mode in WBr_6. If this assignment is correct, these results provide the first spectroscopic data on a binary transition metal hexabromide.

At higher temperatures, when the stoicheiometry of the solid approaches WBr_5, it appears that a single species is evolved, characterised by two i.r.-active bands at 280 and 245 cm^{-1}. Taking into consideration both the mass spectrometric data on WBr_5, and the previous matrix studies on WCl_5, we propose that the absorptions at 280 and 245 cm^{-1} are due to the A_2'' and E' W–Br stretching modes respectively in D_{3h} WBr_5.

Conclusions

This work has demonstrated first that matrix isolation provides a very convenient route for obtaining good quality i.r. and u.v.-visible data on WCl_6 under conditions demonstrably free from significant $WOCl_4$ impurity. As a result, it is possible to assign the charge-transfer bands with some confidence. Secondly, the i.r. studies on tungsten(V) chloride indicate that the vapour is predominantly monomeric, and that monomeric WCl_5 has D_{3h} symmetry. If this conclusion is correct, it provides support for the Raman study on molecular $MoCl_5$, over that offered by electron diffraction. Related experiments on the binary tungsten–bromine system yielded i.r. absorptions which are assigned to WBr_6 and WBr_5, with molecular symmetries O_h and D_{3h} respectively.

Acknowledgements

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