Infrared and Electronic Spectra of Matrix-isolated Chromium(V) Trichloride Oxide

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This paper describes the characterisation of molecular $CrOCl_3$ by i.r., u.v.–visible, mass, and e.s.r. spectroscopy. In particular, argon-matrix spectra yield i.r. stretching fundamentals at 1 018.0, 462.0, and 410.0 cm^{-1} for the most abundant species $^{52}CrO^{35}Cl_3$ (C_{3v}). A vibrational analysis for the remaining prominent isotopomers confirms this assignment, and gives an estimate of *ca.* 105° for the ClCrCl angle. The lowest-energy *d–d* transition in the corresponding u.v.–visible spectrum is observed at 12 970 cm^{-1}, and the intense colour of $CrOCl_3$ arises principally from charge-transfer bands at 40 816, 31 250, 27 770 (sh), and 22 123 cm^{-1}.

CHROMIUM(V) is a rare oxidation state.[1] Our knowledge of neutral complexes is limited to the red pentafluoride CrF_5,[2] the trichloride oxide $CrOCl_3$,[3] and the trifluoride oxide $CrOF_3$[4] which has never been obtained in pure form, and all these species are rather poorly characterised. The only detailed studies for this oxidation state involve complexes in which the chromium is in an anion, and these include the chromates(V) $M_3[CrO_4]$ (M = Li, Na, K, Rb, or Cs),[5] the tetraperoxochromate(V) $K_3[CrO_8]$,[6] and various halogenochromates such as $K[CrOF_4]$,[7] $[NEt_4]_2[CrOF_5]$,[8] $[AsPh_4][CrOCl_4]$, and $Cs_2[CrOCl_5]$.[8-11]

In this paper we report the results of the first detailed study on a neutral chromium(V) compound, $CrOCl_3$. This compound was originally prepared by Krauss and co-workers,[3] but the only properties reported in addition to analysis figures were a magnetic moment ($\mu_{eff.} = 1.8$ B.M.) † and a u.v.–visible spectrum in acetic acid solution. A preliminary report has also recently appeared [12] describing vapour-phase photoelectron spectral studies on this molecule. Here we present high-resolution i.r. and u.v.–visible spectral data for matrix-isolated $CrOCl_3$, in addition to mass-spectrometric and solution e.s.r. measurements.

RESULTS AND DISCUSSION

Preparation of $CrOCl_3$.—Chromium trichloride oxide was prepared from chromyl chloride (CrO_2Cl_2) and boron trichloride using the method outlined by Krauss and co-workers.[3] The synthesis was carried out in a conventional glass vacuum line fitted with greaseless joints and taps, and it was necessary to flame the system thoroughly before use. Freshly distilled CrO_2Cl_2 (1 cm^3) and BCl_3 (20 cm^3) were condensed into a U tube at 77 K, and the mixture was then allowed to warm up slowly to 273 K and maintained at this temperature for 18 h. At the end of this period the contents of the reaction vessel were deep red-brown in colour, and volatile material (excess of BCl_3, traces of CrO_2Cl_2, and some Cl_2) was removed. The U tube was then warmed to room temperature, and the desired product sublimed *in vacuo* (*ca.* 10^{-6} bar) and condensed at 273 K as an almost black deposit. Towards the end of the sublimation, the U tube was gently warmed to *ca.* 320 K to remove all traces of product. This preparative route gave a yield of $CrOCl_3$ *ca.* 50% (based on CrO_2Cl_2) and the product could be stored indefinitely in rigorously dry glass ampoules at *ca.* 263 K with no obvious signs of decomposition. The material could also be repeatedly resublimed *in vacuo* with negligible loss, but storage at room temperature led to slow decomposition with the gradual production of chromyl chloride. Solutions of $CrOCl_3$ in BCl_3, $CFCl_3$, or CCl_4 are similarly stable at low temperatures, but decompose rapidly at room temperature.

Mass Spectroscopy.—Mass spectra of the vapour above samples of $CrOCl_3$ maintained at *ca.* 283 K were recorded on an A.E.I. MS 12 spectrometer using a modified inlet system designed specially for short-lived species. Prominent ion peaks were observed corresponding to $[CrOCl_3]^+$ (*m/e* 173, $I = 68$), $[CrO_2Cl_2]^+$ (*m/e* 154, $I = 89$), $[CrOCl_2]^+$ (*m/e* 138, $I = 75$), $[CrO_2Cl]^+$ (*m/e* 119, $I = 87$), and $[CrOCl]^+$ (*m/e* 103, $I = 100$). The presence of $[CrO_2Cl_2]^+$ in these spectra is believed to arise from CrO_2Cl_2 produced by thermal decomposition of $CrOCl_3$ prior to ionisation, as the relative intensity of the peak at $m/e = 154$ increased markedly as the temperature of the source block rose above *ca.* 400 K.

E.S.R. Spectroscopy.—E.s.r. spectra were recorded on a Varian E3 machine using *X*-band. At 273 K the signal obtained from a dilute solution of $CrOCl_3$ in CCl_3F solvent consisted of a single line at $g = 1.989 \pm 0.002$. This value may be compared with those reported [9] for $[CrOCl_4]^-$ ($g = 1.988$) and $[CrOCl_5]^{2-}$ ($g = 1.970$).

Infrared Spectroscopy.—Infrared spectra of $CrOCl_3$ were obtained over the range 200—4 000 cm^{-1} both for solid samples at *ca.* 250 K and for matrix-isolated samples at *ca.* 12 K. In both types of experiment, the vapour above freshly sublimed $CrOCl_3$ maintained at *ca.* 273 K was slowly condensed onto a CsI window cooled to the appropriate temperature by an Air Products Displex unit. Deposition times were typically *ca.* 1 h, and in the matrix-isolation experiments the dilution factor due to the inert gas (research-grade Kr or Ar) was estimated to be in excess of 1 000. The general features of our matrix-isolation apparatus are described elsewhere.[13] The principal aim of these i.r. studies was to obtain high-quality spectra which could be used first to characterise $CrOCl_3$ and secondly to provide, through isotope pat-

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 bar = 10^5 Pa; 1 dyn = 10^{-5} N.

terns, information regarding the symmetry and approximate geometry of the isolated molecule.

Matrix-isolation studies. When $CrOCl_3$ vapour was condensed with an excess of inert gas at 12 K, the resulting i.r. spectrum showed two prominent bands at *ca.* 1 020 and 462 cm^{-1} and a weaker feature at *ca.* 410 cm^{-1}. No bands due to CrO_2Cl_2 were observed.[14] The mass spectroscopic data clearly point to the existence of molecular $CrOCl_3$ in the vapour phase under these spray-on conditions, and a preliminary band assignment may be made by reference to the i.r. spectra of $VOCl_3$ [15a] and $AsOCl_3$.[15b] In liquid $VOCl_3$ (C_{3v}), the fundamental stretching vibrations lie at 1 035 [A_1, ν(V–O)], 504 [E, ν(V–Cl)], 408 cm^{-1} [A_1, ν(V–Cl)], with bending modes at 249 (E), 165 (A_1), and 129 (E) cm^{-1}. By analogy, the three bands observed here for $CrOCl_3$ are assigned as 1 020 [A_1, ν(Cr–O)], 462 [E, ν(Cr–Cl)], and 410 cm^{-1} [A_1, ν(Cr–Cl)]. Prolonged deposition resulted in the parallel growth of these features, and although we anticipated the appearance of perhaps one lower-frequency bending mode this was not located. The above assignment for the stretching modes in $CrOCl_3$ is confirmed by the isotope patterns observed under high resolution.

Observed and calculated vibration bands (cm^{-1}) for matrix-isolated chromium trichloride oxide $CrOCl_3$

Obs.[a]		Calc.[b]		Assignment[c]	
Krypton	Argon	I	II		
site A 1 022.3	1 023.2	1 023.1	1 023.2	$^{50}Cr^{16}OCl_3$	ν(Cr–O) (A_1)
(site B)	(1 026.8)				
site A 1 017.3	1 018.0	1 018.0	1 018.0	$^{52}Cr^{16}OCl_3$	
(site B) (1 020.0)	(1.021.5)				
site A 1 014.8	1 015.6	1 015.6	1 015.6	$^{53}Cr^{16}OCl_3$	
site A 1 012.5	1 013.4	1 013.3	1 013.2	$^{54}Cr^{16}OCl_3$	
460	462	462.0	462.0	$^{52}CrO^{35}Cl_3$	ν(Cr–Cl) (E)
(isotope structure not resolved)		460.0	459.9	$^{52}CrO^{35}Cl^{37}Cl_2$	
		457.8	457.7	$^{52}CrO^{35}Cl_2{}^{37}Cl$	
		455.4	455.2	$^{52}CrO^{37}Cl_3$	
407.5	410.0	410.0	410.0	$^{52}CrO^{35}Cl_3$	ν(Cr–Cl) (A_1)
404.4	406.9	406.5	406.8	$^{52}CrO^{35}Cl_2{}^{37}Cl$	
401.4	403.9	403.3	403.8	$^{52}CrO^{35}Cl^{37}Cl_2$	
		400.4	401.1	$^{52}CrO^{37}Cl_3$	

[a] Accuracy ±0.3 cm^{-1}. [b] Prominent isotope features only. Calculation I assumes ClCrCl 109° 28′ and F(Cr–O) = 7.40, F(Cr–Cl) = 2.54, and F(Cr–Cl, Cr–Cl) = 0.22 mdyn Å^{-1}. Calculation II assumes ClCrCl 105°, and corresponding force constants 7.38, 2.52, and 0.14 mdyn Å^{-1}. Values fitted to argon-matrix frequencies of $^{52}CrO^{35}Cl_3$. [c] Symmetry labels in parentheses refer to C_{3v} species. Where no isotope mass is specified, the corresponding frequency is insensitive to mass changes in that isotope.

Figure 1(*a*) shows the argon-matrix bands at *ca.* 1 020, *ca.* 462, and *ca.* 410 cm^{-1} under high resolution, whilst Figure 1(*b*) shows the corresponding bands using krypton as the matrix material. The frequencies of the individual components are given in the Table. Although the band at *ca.* 462 cm^{-1} shows no resolvable fine structure, it is evident that both the other bands show splittings which could be due to the natural abundance of chromium and/or chlorine isotopes. In particular, the argon-matrix feature at *ca.* 410 cm^{-1} shows a well resolved triplet at 410.0, 407.0, and 404.0 cm^{-1} with intensity ratio close to 3 : 3 : 1. In krypton, corresponding peaks are observed at 407.5, 404.4, and 401.4 cm^{-1} This pattern of intensities corresponds very closely to the three most intense components of the characteristic quartet pattern expected for the A_1 stretching mode of a pyramidal MCl_3 unit.[16] For a ^{35}Cl : ^{37}Cl abundance ratio of *ca.* 3 : 1, simple statistics would predict four bands with relative intensity *ca.* 27 : 27 : 9 : 1, and as the natural abundance of chromium isotopes is 4.3% ^{50}Cr, 83.8% ^{52}Cr, 9.5% ^{53}Cr, and 2.4% ^{54}Cr it is evident that only one metal isotope, ^{52}Cr, will contribute significantly to this pattern. The fine structure for the A_1 Cr–O stretch at *ca.* 1 020 cm^{-1} will, in contrast, show a negligible chlorine-isotope effect, and, as a result, the high-resolution spectrum should consist of a single intense band corresponding to ^{52}Cr–O with three weaker satellites for ^{50}Cr, ^{53}Cr, and ^{54}Cr. Neither Figure 1(*a*) nor 1(*b*) shows this simple pattern in the region of 1 020 cm^{-1}, but both spectra may be interpreted if one recognises the possibility of different trapping sites in the matrix. This would result in a superposition of chromium-isotope patterns producing an apparently complex multiplet. Support for this interpretation comes from the fact that it is possible to reproduce the observed patterns in argon and krypton assuming two sites A and B, and that in krypton there is a marked preference for site A.

Although we were not able to obtain a complete set of vibrational fundamentals, it is possible to estimate all the isotope shifts expected for the stretching modes in $CrOCl_3$ with a reasonable accuracy using the ' high-frequency separation ' approximation.[14] The Table shows the results of two typical force-constant calculations in which we have assumed that the stretching modes may be satisfactorily reproduced by retaining two principal force constants, F(Cr–O) and F(Cr–Cl), and one interaction constant F(Cr–Cl, Cr–Cl). The only additional parameter required for a routine solution of this problem using the Wilson GF matrix method is the bond angle ClCrCl, and in calculation I (Table) this is set at the tetrahedral value of 109°28′. Values for the three force constants are obtained from the (site A) argon-matrix frequencies of $^{52}CrO^{35}Cl_3$, and these parameters are then used to recalculate the frequencies of all the isotopic combinations. The agreement between observed and calculated frequencies for ν(Cr–O) is very satisfactory, but there is a small cumulative error in the chlorine-isotope shifts for the band at 410 cm^{-1}. By choosing the slightly smaller value of 105° for the ClCrCl angle, this discrepancy is essentially removed, and the isotope calculations for this geometry are summarised under calculation II. The agreement between these observed and calculated isotope frequencies is clearly very satisfactory, but a problem remains concerning the E mode at *ca.* 462 cm^{-1}, where we were unable to resolve any isotope splitting. Figure 1(*c*) summarises, in line form, the isotope patterns computed for all three observed fundamentals, and predicts that this band should show an ' anomalous ' quartet pattern similar to that observed for the degenerate modes of other metal trichlorides.[13,16] Two factors may contribute to the overall broadening of this band. First, the existence of two trapping sites may result in two overlapping quartets separated by *ca.* 1.5 cm^{-1}. This would effectively prevent resolution, but if this were the prime reason one might expect the A_1 mode at *ca.* 410 cm^{-1} to be similarly affected. The second possibility seems more likely: with two trapping sites, it would be optimistic to suppose that both of these would preserve a C_{3v} environment for the isolated molecule, and it is likely that in at least one of these sites the degeneracy of the E mode might be lifted. This would result in broadening of the band at *ca.* 462 cm^{-1}, but would not affect the A_1 stretch at *ca.* 410 cm^{-1}.

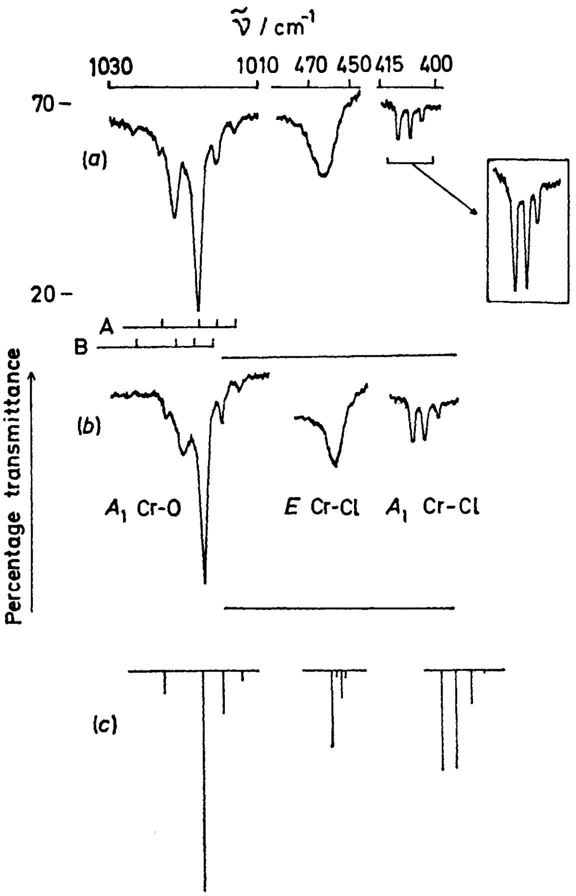

FIGURE 1 Infrared stretching modes of $CrOCl_3$: (*a*) argon-matrix spectrum under high resolution (inset: extended deposition); (*b*) krypton-matrix spectrum; (*c*) computed isotope patterns for principal species

These matrix experiments therefore establish the identity of the trapped species as molecular $CrOCl_3$ with C_{3v} symmetry, with an estimated ClCrCl angle of *ca.* 105°. However, in view of the assumptions inherent in the above calculation, we would place an uncertainty of at least $\pm 5°$ on this value.

Spectrum of solid $CrOCl_3$. In addition to the matrix studies described above, i.r. spectra were also obtained for $CrOCl_3$ condensed directly from the vapour phase onto the cold window. Although the spectra of these deposits showed some similarity to the matrix experiments, there were also important differences. At *ca.* 250 K the spectrum of the solid typically showed *four* bands at 1 024vs, 435m(sh), 408vs,br, and 333s cm^{-1}. The band at 1 024 cm^{-1} clearly corresponds to the terminal Cr–O stretch, but in the Cr–Cl stretching region we observe *three* prominent bands at significantly lower frequencies than those found in the isolated molecule. This suggests that simple monomeric units are no longer present, and may in turn account for the surprisingly low volatility of $CrOCl_3$ compared with CrO_2Cl_2 or $VOCl_3$. It is interesting to note that $MoOCl_3$ has been found to be polymeric in the solid, with terminal Mo–O bonds and extensive chloride bridging,[17] and the spectrum observed here for solid $CrOCl_3$ is consistent with a similar association *via* halide bridging.

Electronic Spectra.—Krauss and co-workers [3] reported the electronic spectrum of $CrOCl_3$ in acetic acid solution to contain bands at 25 640 and 19 160 cm^{-1}. Our own attempts to obtain spectra in CCl_4 or $CFCl_3$ at 273—283 K gave poor quality bands which changed with time, rapidly developing the characteristic features of CrO_2Cl_2 spectra in these solvents. In order to obtain a reliable electronic spectrum we therefore carried out a number of experiments in low-temperature matrices.

The u.v.–visible absorption spectra of $VOCl_3$ and $CrOCl_3$ in argon matrices were recorded in the range 200—850 nm (50 000—11 000 cm^{-1}). Matrices were formed by co-depositing $CrOCl_3$ vapour (sample held at 258—263 K) and argon onto a LiF window held at 10 K,[18] or, in the case of $VOCl_3$, by pulsed deposition. For $CrOCl_3$, prominent bands were observed at 40 816, 31 250, 27 770(sh), 22 123, and 20 000(sh) cm^{-1} and a weak band at 12 970 cm^{-1} [Figures 2(*b*)—2(*d*)], and the four highest-frequency features in particular correlate with the $VOCl_3$ bands at 48 076, 40 322, 34 482(sh), and 29 940 cm^{-1} [Figure 2(*a*)]. The molecular orbital (m.o.) diagrams proposed for $VOCl_3$ [19] and $MnOCl_3$ [20] suggest that the unpaired electron in $CrOCl_3$ will occupy an orbital of *e* symmetry and that the lowest unoccupied orbital also has *e* symmetry. By comparison with the spectrum for d^0 $VOCl_3$, the band at 12 970 cm^{-1} can be assigned to the *d–d* transition between these two levels, which gives a crystal-field splitting parameter $\Delta = 12\,970$ cm^{-1}, and the shoulder at 20 000 cm^{-1} is probably the second *d–d* band expected [1,21] for $[CrO]^{3+}$ complexes, although we note that an alternative assignment has recently been proposed for the second band in the spectrum of the $[CrOCl_4]^-$ ion.[10] The higher-energy bands are clearly charge-transfer transitions and our tentative assignment below is based upon a consideration[22] of the charge-transfer (c.t.) energies and optical electronegativaties for a range of related species: $MnOCl_3$,[20] $[CrOCl_4]^-$,[10] $[CrOCl_5]^{2-}$,[1] and $[CrO_4]^{3-}$.[1] We propose that the band at 40 816 cm^{-1} is O→M c.t., that at 22 123 cm^{-1} is Cl→M c.t., whilst the band at 31 250 and the shoulder at 27 770 cm^{-1} have both O→M and Cl→M c.t. components. Under high resolution the band at 22 123 cm^{-1} showed fine structure which resembles that on the long-wavelength absorption bands of matrix-isolated CrO_2Cl_2 (24 500 and 19 230 cm^{-1})[23,24] and the long-wavelength excitation band of matrix-isolated CrO_2Cl_2.[25] The fine structure for CrO_2Cl_2 has been assigned[25] as arising from the Cl–Cr–Cl bending and Cr–Cl stretching modes.

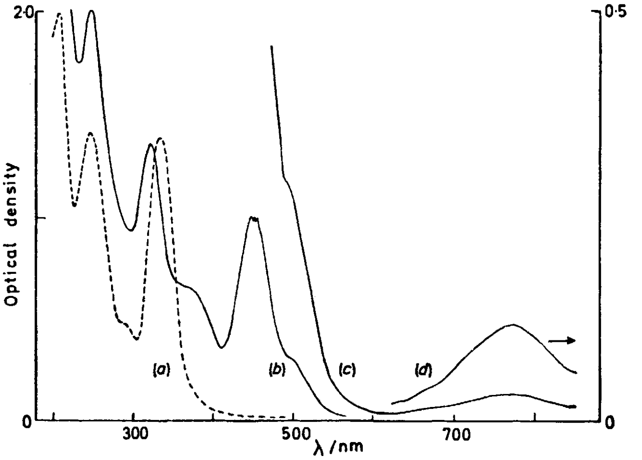

FIGURE 2 Ultraviolet-visible absorption spectra for $VOCl_3$ and $CrOCl_3$ in argon matrices at 10 K: (*a*) $VOCl_3$, pulsed deposition (*ca.* 1 : 200); (*b*) $CrOCl_3$, after 28 min slow spray on; (*c*) as (*b*), after another 80 min deposition; (*d*) as (*c*) but with four-fold ordinate expansion for the long-wavelength band

However, unlike CrO_2Cl_2, for which emission spectra have been obtained for the matrix-isolated molecule,[23-25] no emission was detected on excitation of $CrOCl_3$ in any of the absorption bands. This may arise because of the possibility for $CrOCl_3$ of c.t.↔*d–d* intersystem crossing followed by radiationless decay from the *d–d* states, whereas CrO_2Cl_2 as a d^0 system does not have this possibility. This interpretation has been substantiated by the fact that matrix-isolated $VOCl_3$ shows weak emission spectra at *ca.* 10 K.[24]

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