Synthesis and Properties of Chromium(V) Trifluoride Oxide $CrOF_3$ and Related Oxo-anions †

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Chromium trifluoride oxide has been prepared from CrO_3 and BrF_3, followed by cautious fluorination. It has been characterised by elemental analysis, i.r., u.v.–visible, e.s.r. spectroscopy, and magnetic susceptibility, and a number of its properties are described. The compound $CsCrOF_4$ has been prepared from $Cs_2Cr_2O_7$ and BrF_3 and similarly characterised, but attempts to isolate salts containing the $[CrOF_5]^{2-}$ ion by a variety of methods were unsuccessful.

Impure samples of solid $CrOF_3$, formulated as $CrOF_3$·*ca.* $0.3XF_3$ (X = Br or Cl), were first obtained over 20 years ago,[1,2] by treating CrO_3 with the halogen trifluorides, but attempts to remove the residual XF_3 by heating resulted in complete decomposition. More recently, it has been reported[3] that $CrOF_3$ may be prepared by the reaction of ClF with CrO_3 or CrO_2F_2, and some of its properties have been described. However, this synthetic route yielded adducts of typical stoicheiometry $CrOF_3$·0.1ClF as the initial product, and the residual ClF could only be removed by multiple treatment with F_2 at 120 °C.

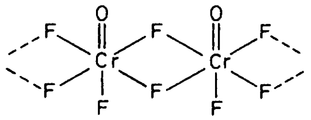
We have recently characterised [4] one of the few [5] chromium(V) compounds, $CrOCl_3$, by a combination of i.r. and u.v.–visible spectroscopy. The present paper describes an alternative synthesis of pure $CrOF_3$, together with some of its properties and reactions, and summarises our attempts to identify the vapour-phase monomer. We also describe the synthesis and characterisation of $CsCrOF_4$, and our attempts to prepare salts containing the $[CrOF_5]^{2-}$ ion.

Results and Discussion

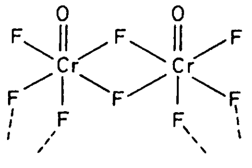
Synthesis of $CrOF_3$.—Our synthesis of $CrOF_3$ consists of treatment of the adduct [2] $CrOF_3$·$0.3BrF_3$ with fluorine under mild conditions, to remove the halogen fluoride. Details of the method are given in the Experimental section. Cautious fluorination to remove BrF_3 has previously been employed in the syntheses of MnF_3[6] and PtF_4.[7] However, it should be noted that $CrOF_3$ *reacts* with fluorine at *ca.* 190 °C to give CrF_5.[3]

We therefore studied the further reaction between $CrOF_3$ and F_2 at both 120 and 160 °C. At the lower temperature there was no apparent reaction, but after heating to 160 °C, samples of $CrOF_3 + F_2$ yielded a brown powder which showed prominent i.r. bands in the Cr=O stretching region at 990 and 1 020 cm^{-1}. The lower-frequency band is due to unreacted $CrOF_3$, but the new band at 1 020 cm^{-1} is characteristic of $CrOF_4$.[8] The overall reaction $CrOF_3 + F_2 \longrightarrow CrF_5 + \frac{1}{2}O_2$ occurring at 190 °C may therefore proceed *via* the intermediate formation of $CrOF_4$.

Physico-chemical Properties.—Pure $CrOF_3$ is a red-purple solid which hydrolyses readily in air, and decomposes instantly, but not violently, in water to produce a yellow-green solution. Our samples reacted vigorously with aqueous NaOH or '880' ammonia to give a yellow solution and a green precipitate according to the disproportionation reaction $3Cr^{V} \longrightarrow 2Cr^{VI} + Cr^{III}$, but $CrOF_3$ dissolves in cold concentrated HCl to give a dark red solution containing the $[CrOCl_5]^{2-}$ ion.[5]



or



Samples were surprisingly unreactive towards organic materials. Although $CrOF_3$ was found to dissolve smoothly, with reaction, in dimethyl sulphoxide, it neither dissolved in nor reacted with dry CCl_4, $CFCl_3$, $(CH_3)_2CO$, CH_3CO_2H, CH_3CN, or even C_2H_5OH, but the presence of small amounts of water resulted in violent reaction with $(CH_3)_2CO$ or C_2H_5OH. Some of these observations conflict with the results of Green *et al.*[3] in that they report a vigorous reaction with $(CH_3)_2CO$ and dimethyl sulphoxide. These differences may be due to some residual halogen fluoride in their material,‡ or may be a further example [9] of the diverse reactivities sometimes found for fluorides synthesised by different routes.

The i.r. spectra of solid $CrOF_3$ showed a strong band at *ca.* 990 cm^{-1} corresponding to ν(Cr=O), and several broad bands in the range 620—480 and at *ca.* 670 cm^{-1} which may be assigned to bridging and terminal Cr–F groups respectively. These observations are in good agreement with the earlier i.r. data reported by Green *et al.*[3] and indicate that our samples of solid $CrOF_3$ are polymeric with a structure perhaps similar to that found for VOF_3,[10] as indicated above.

The magnetic moment of solid $CrOF_3$ at room temperature was found to be $\mu_{eff.} = 1.87 \pm 0.05$ B.M., which is consistent with the presence of (d^1) Cr^V, and the e.s.r. spectrum of the solid showed a single broad line at $g = 1.831$, with no discernible fine structure.

The diffuse reflectance u.v.–visible spectrum of $CrOF_3$ is shown in the Figure (*a*), and has absorptions at 13 600, 19 500(sh), 22 400, 26 500(sh), 31 000, and 37 000 cm^{-1}. If one

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† *Non-S.I. units employed:* B.M. ≈ 9.27×10^{-24} A m^2; atm = 101 325 Pa.

‡ The adduct $CrOF_3$·$0.3BrF_3$ is extremely reactive towards most organic materials.

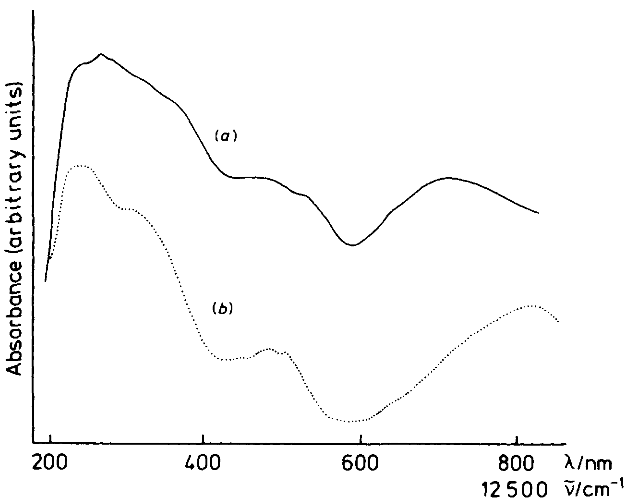

Figure. Diffuse reflectance u.v.–visible spectra of (*a*) solid CrOF$_3$ and (*b*) solid CsCrOF$_4$

assumes a fluorine-bridged octahedral environment for the chromium, the *d*-orbital ordering for local C_{4v} symmetry is expected to be d_{xy} (B_2) < d_{xz}, d_{yz} (E) < $d_{x^2-y^2}$ (B_1) < d_{z^2} (A_1) resulting in a $^2B_2$ ground state. The lowest-energy band at *ca.* 13 600 cm^{-1} is thus assigned as the $^2B_2 \rightarrow {}^2E$ '*d–d*' transition. The positions of the lowest-energy charge-transfer (c.t.) bands may be estimated using a value of *ca.* 2.7 for the optical electronegativity (χ_{opt}) of Cr^{V} in an octahedral environment,[11] and when combined with appropriate values of χ_{opt} for F and O, this model [11] predicts F$\rightarrow$Cr and O$\rightarrow$Cr c.t. bands at *ca.* 36 000 and *ca.* 27 000 cm^{-1} respectively. These predictions provide tentative assignments for the observed bands at 37 000 and 26 500 cm^{-1}, and the only remaining feature of significance is the broad band at 22 400 cm^{-1} and its accompanying shoulder at 19 500 cm^{-1}.

In their study of the u.v.–visible spectrum of [CrOCl$_4$]$^-$ in [AsPh$_4$][CrOCl$_4$] Garner *et al.*[5] also found bands in this intermediate region at *ca.* 21 000—25 000 and at 18 100 cm^{-1}, and suggest that they be assigned to transitions involving Cr–O (π)$\rightarrow$Cr–O (σ^*). This assignment would also seem likely for our CrOF$_3$ bands, since the only reasonable alternative, *viz.* intense higher-energy '*d–d*' transitions, would imply considerable departure from local C_{4v} symmetry.

Finally, attempts were made to obtain spectroscopic data for *molecular* CrOF$_3$ using a combination of Knudsen-cell vaporisation and matrix-isolation i.r. techniques. This approach had previously been very successful in identifying the monomeric species formed during vacuum sublimation of the fluorine-bridged polymers MoOF$_4$ and WOF$_4$.[12] In a typical experiment, a sample of CrOF$_3$ was vaporised from an inductively heated Monel holder, and the effusing species condensed with an excess (>1 000) of nitrogen onto a caesium iodide window maintained at *ca.* 12 K. At sample temperatures of *ca.* 200 °C, the i.r. spectra showed sharp absorptions characteristic [13] of CrO$_2$F$_2$ at 1 014, 1 007, 785, and 722 cm^{-1}. Further heating to *ca.* 350 °C resulted in the growth of these bands, and the appearance of several new features in the Cr–F stretching region (see Experimental section). Many of these additional bands remain unassigned, but two of the most prominent features, at 790.3 and 780.6 cm^{-1}, were identified as fundamentals of CrF$_4$.[8] No firm evidence was obtained, however, for molecular CrOF$_3$, which was expected to have a distinctive ν(Cr=O) mode in the region of 1 000 cm^{-1}.

After cooling from *ca.* 350 °C to room temperature, these heated samples of CrOF$_3$ left a green, powdery residue which proved to be CrF$_3$ from elemental analysis. Samples of pure CrF$_3$ heated in the same apparatus did not give any vapour species at temperatures below *ca.* 600 °C.

Oxofluorochromates(V).—By comparison with their chloro-analogues, salts containing the ions [CrOF$_4$]$^-$ or [CrOF$_5$]$^{2-}$ have attracted little attention. The salt KCrOF$_4$ has been prepared [1–3] from K$_2$Cr$_2$O$_7$ and BrF$_3$, but is variously described as either purple [1] or tan-green,[3] and there is only one report claiming the isolation of a [CrOF$_5$]$^{2-}$ salt: [NEt$_4$]$_2$[CrOF$_5$].[14]

We have prepared a light fawn coloured material by treating powdered Cs$_2$Cr$_2$O$_7$ with an excess of BrF$_3$ in a silica vessel. The initial reaction product was red, but after pumping off the excess of BrF$_3$ and warming *in vacuo* to 100 °C for 2 h, a pale fawn solid was obtained which gave analysis figures consistent with CsCrOF$_4$. This solid has the following properties. It is instantly hydrolysed by water (to Cr^{III} + Cr^{VI}), but is insoluble in all common solvents apart from anhydrous HF. The i.r. spectrum of the solid contains an intense band at 1 005 cm^{-1}, which is unambiguously assigned as ν(Cr=O), a very intense, broad band centred at *ca.* 650 cm^{-1}, assigned as ν(Cr–F)(terminal), and a weaker feature at 505 cm^{-1} assigned as ν(Cr–F–Cr). In these respects, these i.r. data are very similar to those reported [15] for KVOF$_4$, and as the latter is known from *X*-ray studies [16] to contain C_{4v} anions weakly associated *via* F bridges to form infinite chains, a similar structure seems likely for CsCrOF$_4$.

The electronic spectrum [Figure (*b*)] is similar to that found for CrOF$_3$. The lowest-energy band at 12 000 cm^{-1} is assigned to the $^2B_2 \rightarrow {}^2E$ *d–d* transition, whilst the high-energy c.t. bands at 40 700 and 32 000 cm^{-1} correspond reasonably well to the optical electronegativity model for which lowest-energy F$\rightarrow$Cr and O$\rightarrow$Cr transitions are predicted to lie at *ca.* 36 000 and *ca.* 27 000 cm^{-1} respectively. The intermediate features at 20 000 and 21 000 cm^{-1} are assigned as Cr–O ($\pi \rightarrow \sigma^*$) transitions by analogy with CrOF$_3$ and [CrOCl$_4$]$^-$.

The e.s.r. spectrum of the powdered solid showed a single broad resonance at $g = 2.00(3)$.

Attempts to prepare Salts containing [CrOF$_5$]$^{2-}$.—Although e.s.r. spectra of solutions believed to contain [CrOF$_5$]$^{2-}$ have been reported by several workers,[17] the only description of a solid containing this ion is that of the yellow complex [NEt$_4$]$_2$[CrOF$_5$] by Ziebarth and Selbin.[14] However, they do not report any Cr or F analysis data, and their i.r. spectra do not show clear evidence for Cr–F modes. We repeated their reaction of AgF with [NEt$_4$][CrOCl$_4$] in CH$_2$Cl$_2$ as described (*i.e.* in the presence of some water), and obtained a product with similar properties. However, our analyses showed this to contain chlorine, but no fluorine, and we believe the i.r. spectrum is consistent with a mixture of chloro-anions of Cr^{V} and Cr^{VI}.[5,18] Under rigorously anhydrous conditions, the reaction of solid AgF (in excess) with [NEt$_4$][CrOCl$_4$] in CH$_2$Cl$_2$ is very slow and only partial replacement of chlorine was achieved even after several days.

The preparation of Cs$_2$CrOF$_5$ was attempted by several routes including Cs$_2$CrO$_4$ + BrF$_3$, Cs$_2$CrOCl$_5$ + BrF$_3$, and 2CsF + CrOF$_3$ in anhydrous HF. The first two routes involved a similar sequence of operations to those outlined in the preparation of CrOF$_3$ and CsCrOF$_4$, whilst for the third route an intimately mixed sample of CrOF$_3$ and CsF (1 : 2 molar ratio) was placed in a Monel container and an excess of anhydrous HF condensed onto it. After allowing to stand at room temperature for 24 h, with occasional shaking, the HF was removed and the solid product dried *in vacuo* at

100 °C. Careful examination showed this to be an inhomogeneous fawn powder, and its i.r. spectrum showed bands characteristic only of $CsCrOF_4$ and $CsHF_2$.[19] Examination of the products from the BrF_3 reactions by elemental analysis and i.r. spectroscopy showed that equimolar amounts of $CsCrOF_4$ and $CsBrF_4$ [20] had been formed.

Although the preparation of $[CrOF_4]^-$ salts is therefore straightforward, we have found no evidence that compounds containing the $[CrOF_5]^{2-}$ ion can be obtained in the solid state.

Conclusions

Many of the measurements described in this paper have depended on the routine synthesis of gram quantities of pure $CrOF_3$, and some of these results provide a striking example of the differences between transition-metal fluoride oxide species and their corresponding chloride oxides. Thus, whereas $CrOCl_3$ and $[CrOCl_4]^-$ may be reasonably accurately described as monomeric species, $CrOF_3$ and $[CrOF_4]^-$ show properties associated with extensive polymerisation: notably,[21] involatility and insolubility, and characteristic metal–halogen absorptions in both bridging and terminal regions of the i.r. spectrum. The electronic and e.s.r. spectra are relatively insensitive to these structural differences, but are consistent with a C_{4v} chromium environment in both $CrOF_3$ and $[CrOF_4]^-$.

Experimental

General details of the techniques and equipment used in the various physicochemical studies on $CrOF_3$ and $[CrOF_4]^-$ salts have been described elsewhere.[22] Fluorine analyses were carried out using the lanthanum–alizarin complexone * method,[23] whilst chromium was determined spectrophotometrically at pH = 10 as $[CrO_4]^{2-}$ after hydrolysis and oxidation with H_2O_2.

Synthesis of $CrOF_3$.—Our synthesis of $CrOF_3$ is an extension of the method initially proposed by Clark and Sadana.[2] In a typical preparation, BrF_3 (*ca.* 15 cm^3) which had been purified by distillation was condensed onto powdered CrO_3 (*ca.* 2.5 g) at −196 °C in a silica ampoule fitted with a polytetrafluoroethylene tap. Slow warming to room temperature produced a deep red solution, and further warming to *ca.* 40 °C resulted in complete reaction. The excess of BrF_3 was then distilled off, to leave a purple product. This material has the approximate stoicheiometry $CrOF_3{\cdot}0.3BrF_3$, and after removal from the reaction tube it was powdered in a dry-box and loaded into a Monel autoclave (300 cm^3). After filling with F_2 to 1 atm pressure, the autoclave was heated at 120 °C for 16 h. After cooling, the autoclave was evacuated and the fluorination repeated once more. The final product was a dark red-purple solid which contained no bromine and gave satisfactory fluorine and chromium analyses. The yield was typically *ca.* 90% (Found: Cr, 41.7; F, 45.7. Calc. for CrF_3O: Cr,41.6; F, 45.6%). Principal i.r. bands: 990, 670, 580vs, 485m, and 295m cm^{-1}. U.v.-visible bands: 13 600, 19 500(sh), 22 400, 26 500(sh), 31 000, and 37 000 cm^{-1}. E.s.r. of solid: $g = 1.831$. Samples of $CrOF_3$ were handled in a dry-box, and stored in stainless-steel containers.

Vaporisation of $CrOF_3$.—Final green product (Found: F, 51.9. Calc. for CrF_3: F, 52.3%). I.r. bands: (*a*) initial (N_2 matrix) 1 014, 1 007, 785, and 722 cm^{-1} (CrO_2F_2); (*b*) on further heating 790·3 and 780·6 (CrF_4), 796, 732, 707, and 675 cm^{-1}.

Properties of $CsCrOF_4$.—(Found: Cr, 19.2; F, 27.7. Calc. for $CrCsF_4O$: Cr, 18.8; F, 27.4%). I.r. bands: 1 005vs, 650vbr, and 505w cm^{-1}. U.v.-visible bands: 12 000, 20 000(sh), 21 000, 32 000, and 40 700 cm^{-1}.

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* *N*-Carboxymethyl-*N*-[(9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenyl)methyl]glycine.