Tetrachloro-oxo-osmium(VI): a New Synthesis, and Matrix-isolation Infrared and Ultraviolet–Visible Studies

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Pure samples of $OsOCl_4$ have been prepared by a new synthetic route involving OsO_4 and BCl_3. The i.r. spectrum in low-temperature matrices has been obtained, and exhibits characteristic bands at 1 032 and 395 cm^{-1}. These are assigned as ν_{A_1}(Os=O) and ν_E(Os–Cl) in a C_{4v} model for monomeric $OsOCl_4$. The electronic spectrum has also been recorded under similar conditions, and tentative assignments proposed for the most intense absorptions.

Very few oxide chlorides have been reported for the platinum metals: a situation which is in marked contrast to the chemistry of earlier 4*d* and 5*d* metals. In the case of osmium, several oxide fluorides have been characterised,[1] but the only known oxide chloride is $OsOCl_4$, which has been obtained either by oxychlorination of osmium metal [2] or as one of the products in the reaction between OsO_4 and $SOCl_2$.[3] The structure of $OsOCl_4$ in the solid state is unknown, but its low melting point (32 °C) [2] suggests that it probably exists as weakly associated monomers, thus resembling $ReOCl_4$.[4] The mass spectrum [5] indicates that the vapour is monomeric, and an i.r. spectrum of the vapour, although complicated by sample decomposition,[6] also suggests the presence of monomers.

As part of our studies on a series of transition-metal oxide halides (*e.g.* $CrOCl_3$ [7] and MOX_4 [8]) we report here the high-resolution i.r. and electronic spectra of matrix-isolated $OsOCl_4$.

Experimental

Synthesis of $OsOCl_4$.—Osmium tetrachloride oxide is conveniently obtained in high yield from the reaction between osmium tetraoxide and boron trichloride at room temperature. In a typical preparation, OsO_4 (1 g) was placed in an ampoule attached to an all-glass vacuum line, and an excess of BCl_3 (*ca.* 3 cm^3) condensed onto it in small portions (0.5—1.0 cm^3) at −196 °C. The ampoule was allowed to warm up in an ice–salt bath and then subsequently to room temperature, whereupon the solution became reddish brown. After 24 h at room temperature, volatile materials (BCl_3 and Cl_2) were removed *in vacuo*; the product could subsequently be sublimed *in vacuo* by gentle heating and was stored in break-seal ampoules.

The compound is a reddish brown solid (yellow-brown in thin films) which melts to a brown liquid on gentle warming. It is decomposed by moisture to OsO_4 and a black involatile residue, and is reduced by organic matter. However, it may be manipulated readily in all-glass systems using break-seal techniques, although precautions should be taken to avoid extended exposure to light. Typical analysis: Cl, 40.0 (calc.: 40.75%).

Matrix-isolation Studies.—The apparatus used to obtain matrix-isolated samples of $OsOCl_4$ has been described elsewhere.[8] In this work, samples were deposited from a 0 °C bath for both i.r. and u.v.–visible studies, and spectra were recorded on Perkin-Elmer 225 and Nicolet 7199 instruments (i.r.) and on a Pye Unicam SP 1800B spectrometer (u.v.–visible).

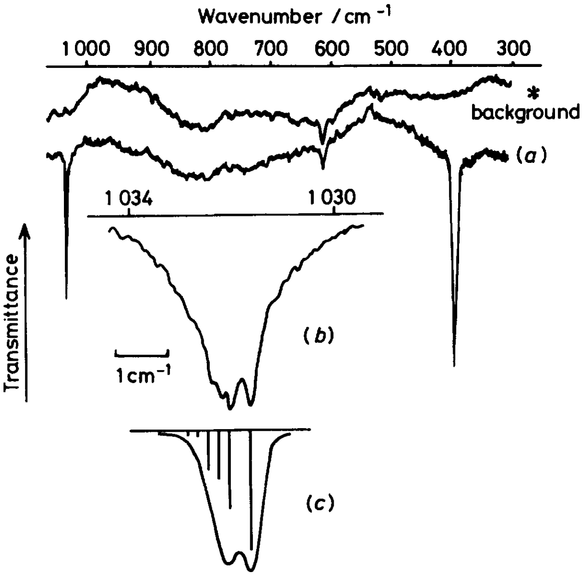

Figure 1. (*a*) Nitrogen-matrix i.r. spectrum (1 100—300 cm^{-1}) of $OsOCl_4$; (*b*) high-resolution spectrum (1 034.5—1 029.5 cm^{-1}) of ν(Os=O); (*c*) calculated band positions for Os=O diatomic unit showing pattern due to natural isotope abundance of osmium and (overlaid) calculated spectrum assuming a gaussian line shape with a (half-height) band width of 0.18 cm^{-1}

Results and Discussion

Infrared Spectra.—The i.r. spectrum of $OsOCl_4$ isolated in a nitrogen matrix shows prominent absorptions centred at 1 032 and 395 cm^{-1}. These may be compared with the gas-phase fundamentals at 1 028 and 397 cm^{-1} assigned to this molecule by Barraclough and Kew.[6] A typical matrix spectrum is shown in Figure 1(*a*), and the similarity between this system and the previously reported spectra of $MoOCl_4$ and $WOCl_4$ [8] leads to an assignment of these bands as 1 032 cm^{-1}, A_1(Os=O), and 395 cm^{-1}, E(Os–Cl), for a C_{4v} geometry.

Under high resolution, both these bands exhibit fine structure which we believe is due to isotope effects. Figure 1(*b*) shows the 1 032 cm^{-1} band at an instrument resolution of 0.06 cm^{-1} and the accompanying computed spectrum [Figure 1(*c*)] shows the envelope expected for an Os=O mode at this frequency taking into account the natural abundance of

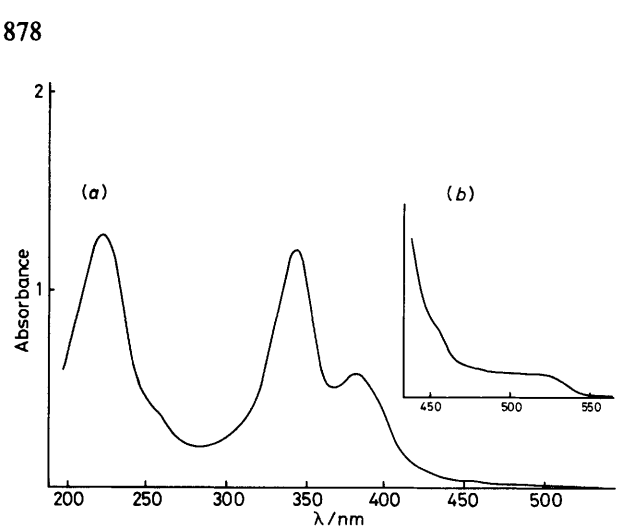

Figure 2. Electronic absorption spectrum of $OsOCl_4$ in a nitrogen matrix at 12 K: (*a*) 200—550 nm, (*b*) 450—550 nm region after further deposition

osmium isotopes and assuming a linewidth of 0.18 cm^{-1}. The agreement is satisfactory. The band at 395 cm^{-1} shows a very complicated pattern under high resolution, as might be anticipated in view of the plethora of isotopomers which are expected to make independent contributions to this mode. Although it was not possible to attempt an analysis of this band, it was qualitatively similar to the *E*(W–Cl) mode previously noted for $WOCl_4$.[8]

These experiments thus establish the existence of monomeric $OsOCl_4$ isolated in a low-temperature matrix, and in contrast to the gas-phase measurements,[6] no problems were experienced due to sample decomposition.

It is also interesting to note that the i.r. spectrum of *solid* $OsOCl_4$ deposited in the absence of the matrix showed moderately sharp (*ca.* 15 cm^{-1}) bands at 1 028 and 392 cm^{-1} indicating the presence of essentially monomeric units.

Electronic Spectra.—The u.v.–visible spectrum of $OsOCl_4$ has not been reported previously, and the only available data on a related osmium(VI) oxo-chloro-species refer to the D_{4h} anion $OsO_2Cl_4{}^{2-}$,[9] for which charge-transfer bands have been assigned at 300 and 270 nm, with a *d–d* band at 500 nm. Figure 2(*a*) shows a typical u.v.–visible spectrum obtained for $OsOCl_4$ isolated in a nitrogen matrix, where major absorptions are present at [nm (cm^{-1})] 225.0 (44 445), 255 (sh) (39 215), 343.0 (29 155), and 386.0 (25 905). After extensive deposition, several very weak absorptions were discernible at *ca.* 460 (21 740), 488 (20 500), and 530 (18 870) and these are shown in Figure 2(*b*). These weaker features are estimated to be *ca.* 1% as intense as the major absorptions, and are tentatively assigned as *d–d* transitions, whilst the intense higher-energy bands are assigned as charge transfer.

Solid $OsOCl_4$ is diamagnetic,[2] and since the i.r. spectrum of the low-temperature solid is similar to that for the matrix-isolated monomer, it is reasonable to suppose that the molecule is also diamagnetic. Assuming a C_{4v} geometry, the *d*-orbital configurations would then be $d_{xy}{}^2(b_2) < d_{xz}{}^0,d_{yz}{}^0(e) < d_{x^2-y^2}{}^0(b_1) < d_{z^2}{}^0(a^1)$, giving a $^1A_1$ ground state. The charge-transfer (c.t.) bands may, in principle, be assigned in two ways, using the results of SCF–Xα–SW calculations, or the optical electronegativity formula. A schematic molecular-orbital energy-level diagram based upon the results of SCF–Xα–SW calculations [10–12] for $MoOCl_4$ and $WOCl_4$ was employed in our spectral analysis [8] for these systems, and may in principle be applied to $OsOCl_4$ by filling the $2b_2$ level (d_{xy}). Unfortunately, however, none of the c.t. bands in this system showed vibrational fine structure which might lead to specific assignments.

The optical electronegativity approach, taking $\chi_{opt}(Os^{VI})$ as 2.6,[13] predicts the lowest theoretical Cl→Os c.t. band at *ca.* 12 000 ± 3 000 cm^{-1} and O→Os at 18 000 ± 3 000 cm^{-1}. However, since the lowest-energy *d* orbital is filled ($d_{xy}{}^2$) the lowest possible transitions will be to $d_{xz},d_{yz}(e)$ and these values must therefore be increased by Δ_1, the $d_{xy} - d_{xz},d_{yz}$ separation. Although there are no experimental data for osmium oxo-chlorides which might provide an estimate of Δ_1, the iso-electronic ion $OsNCl_4{}^-$ has recently been studied in detail, and the electronic spectra assigned from polarised single-crystal spectra.[14] This study estimates Δ_1 as *ca.* 31 000 cm^{-1}, whilst an earlier analysis suggests a value *ca.* 26 000 cm^{-1}.[15] Since the π-antibonding effect of oxide will be significantly less than that of nitride the value of Δ_1 in $OsOCl_4$ could well lie in the range 15 000—20 000 cm^{-1}. On this basis, we propose that the intense bands observed at 25 905 and 29 155 cm^{-1} be assigned as Cl → Os c.t., and that at 39 215 cm^{-1} to O → Os.

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