

## Mixed Bromide-Chlorides of Tungsten(vi)

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The compound  $\text{WOCl}_3\text{Br}$ , prepared by reaction of bromine gas with potassium tri- $\mu$ -chloro-hexachloroditungstate(III),  $\text{K}_3\text{W}_2\text{Cl}_9$ , has been characterized. It was one of a mixture of products which were separated by fractional sublimation. Small deviations in the stoichiometry were consistent with the formula  $\text{WOCl}_n\text{Br}_{4-n}$ , and the compounds were isostructural with  $\text{WOCl}_4$  and  $\text{WOBr}_4$ . X-Ray data and far-i.r. spectra are reported.

PREVIOUS workers<sup>1</sup> reported that the reaction of  $\text{K}_3\text{W}_2\text{Cl}_9$  with bromine vapour at  $450^\circ$  yields the volatile compound  $\text{WCl}_3\text{Br}$ . Since both  $\text{WCl}_4$  and  $\text{WBr}_4$  are involatile, it was surprising that the mixed halide should sublime at  $135^\circ$  in a stream of nitrogen. The reaction was therefore re-investigated in an attempt to further characterize the product and to establish its structure. The work resulted in the isolation of the new compound  $\text{WOCl}_3\text{Br}$ , and a number of samples which deviated slightly from this formula, but which had the general formula  $\text{WOCl}_n\text{Br}_{4-n}$ . The products were diamagnetic, and contained tungsten in a +6 rather than a +4 oxidation state. The X-ray powder diffraction patterns of all the samples were identical. The compound  $\text{WOCl}_3\text{Br}$  was further characterized by single-crystal X-ray analysis and by i.r. spectroscopy.

**X-Ray Data.**—A single crystal of the mixed halide,  $\text{WOCl}_3\text{Br}$ , was mounted in a sealed capillary and rotation and Weissenberg photographs were taken using copper radiation. Single-crystal rotation and Weissenberg photographs were also taken of  $\text{WOCl}_4$  and  $\text{WOBr}_4$  for comparison (Table 1). The mixed halide was found to be body-centred tetragonal, space group  $I4$ , with two molecules of  $\text{WOCl}_3\text{Br}$  per unit cell, and atomic co-ordinates: W in positions (0, 0, 0) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ; O in positions (0, 0, z) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$ ; and Cl (or Br) in positions ( $u, v, z$ ), ( $-u, -v, z$ ), ( $v, -u, z$ ), ( $-v, u, z$ ),  $(\frac{1}{2} + u, \frac{1}{2} + v, \frac{1}{2} + z)$ ,  $(\frac{1}{2} - u, \frac{1}{2} - v, \frac{1}{2} + z)$ ,  $(\frac{1}{2} + v, \frac{1}{2} - u, \frac{1}{2} + z)$ , and  $(\frac{1}{2} - v, \frac{1}{2} + u, \frac{1}{2} + z)$ . This is the space group in which  $\text{WOCl}_4$  and  $\text{WOBr}_4$  crystallize,<sup>2</sup> and the lattice dimensions of  $\text{WOCl}_3\text{Br}$  are observed to be inter-

mediate between those of these two compounds (Table 1). The structure therefore consists of tungsten oxobromotrichloride molecules joined together in chains along the c-axis through W-O-W links. No superlattice diffraction spots were observed in the photographs taken from

TABLE 1  
Lattice parameters and atomic co-ordinates

	$\text{WOCl}_4$	$\text{WOCl}_3\text{Br}$	$\text{WOBr}_4$
$a_0 (=b_0)$ .....	8.48	8.52	8.96
$c_0$ .....	3.99	3.98	3.93
$u(\text{halogen})$ .....	0.258 *	0.260	0.261 *
$v(\text{halogen})$ .....	0.067 *	0.063	0.072 *
$z(\text{halogen})$ .....	0.079 *	0.082	0.090 *
$z(\text{O})$ .....	0.545	0.55	

\* Data for  $u, v$ , and  $z$  for  $\text{WOCl}_4$  and  $\text{WOBr}_4$  from ref. 2.

TABLE 2

I.r. spectra ( $\text{cm}^{-1}$ )			
$\text{WOCl}_4$	$\text{WOBr}_4$	$\text{WOCl}_3\text{Br}$	Assignment
880s,br	840s,br	860s,br	$\nu(\text{W=O})$
725w,sh		730w,sh	
378vs		387vs	$\nu(\text{W-Cl})$
		368vs	
	330m,sh	342m,sh	? ( $\text{W-Br}$ )
323vs		324s	$\nu(\text{W-Cl})$
	250s,br	254m	$\nu(\text{W-Br})$
	230s,br	234s,br	$\nu(\text{W-Br})$

s = Strong, vs = very strong, m = medium, w = weak, sh = sharp, br = broad.

$\text{WOCl}_3\text{Br}$  crystals, such as would be expected from ordered replacement of chlorine atoms by bromine atoms in the lattice. It seems likely therefore that chlorine and bromine atoms occupy the available halogen-atom sites quite randomly or, alternatively, that the crystal consists of  $\text{WOCl}_3\text{Br}$  molecules stacked in a random fashion.

<sup>1</sup> R. C. Young and R. A. Laudise, *J. Amer. Chem. Soc.*, 1956, **78**, 4861.

<sup>2</sup> H. Hess and H. Hartung, *Z. anorg. Chem.*, 1966, **344**, 157.

The intensities of  $hk0$ ,  $hkl$ , and  $hk2$  reflections were measured by visual comparison with a series of standard spots. These intensities were corrected for Lorentz and polarization factors and compared with structure factors calculated using the atomic co-ordinates above and a scattering factor for the halogen atom which was the weighted mean of the factors for chlorine and bromine. No corrections were made to the observed structure factors for absorption. The  $R$  value obtained for 128 independent  $hk0$ – $hk2$  reflections of  $WOCl_3Br$  was 0.177.

*I.r. Spectra.*—The spectrum of the compound  $WOCl_3Br$  (same bulk sample as used for the single-crystal  $X$ -ray study) was measured over the range 1500–200  $\text{cm}^{-1}$ . For comparison, the spectra of  $WOCl_4$  and  $WOBr_4$  were also recorded over this complete range, since such data were not available in the literature. These results are presented in Table 2. The tungsten–oxygen stretching frequencies are in the same range, as expected. The tungsten–chlorine stretching modes are consistent with  $C_{4v}$  symmetry around the tungsten atom. Thus, two bands ( $A_1 + E$ ) are predicted, and two observed. An unexplained extra band occurs at 342  $\text{cm}^{-1}$  in the spectrum of  $WBr_4$ , and also in the spectrum of the mixed halide. The latter spectrum shows two other features: (a) the number of W–Cl stretching modes is extended to 3, as might be expected if the  $E$ -mode split under a lower symmetry in  $WOCl_3Br$ , and (b) the retention of more than one W–Br mode in the spectrum of the mixed halide suggests that some tungsten atoms are bonded to more than one bromine atom. This would be the case if the bromine atoms were randomly distributed in the lattice.

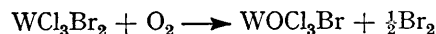
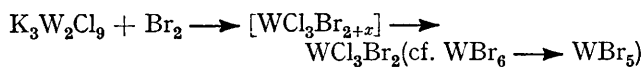
#### DISCUSSION

The  $X$ -ray and i.r. evidence clearly shows that the mixed halide  $WOCl_3Br$  is isostructural with the other oxyhalides,  $WOCl_4$  and  $WOBr_4$ , and there can be no doubt that the analytical identification of this phase is correct.

The origin of oxygen in the system is uncertain, since great care was taken to exclude it. However, there are at least two possibilities. At temperatures of 450°, as used in the preparation, reaction of a gaseous halide with the glass wall cannot be excluded. Secondly, the preparation involves passage of nitrogen for several hours, so that even very small concentrations of adventitious oxygen would be sufficient to react with, say, 1 g. of pure bromo-chloride, if such were the initial product of reaction.

There was good evidence to support such a reaction scheme. In one preparation a paramagnetic, benzene-soluble compound of composition  $WCl_3Br_2$  was obtained as one fraction of the sublimate. Its i.r. spectrum showed no band in the W–O stretching frequency region. In another experiment a similar compound of composition

$WCl_3Br_{2.4}$  was produced. These observations lead us to postulate the following sequence of reactions:



In general, this last reaction would lead to  $WOCl_nBr_{2-n}$  and  $\frac{1}{2}X_2$ . The heats of formation of tungsten chlorides are generally much higher than those of the corresponding bromides,<sup>3</sup> so that reaction of oxygen with  $WCl_3Br_2$  would be expected to yield  $WOCl_3Br$  rather than  $WOCl_2Br_2$ , although some of the latter could also be formed. These compounds would, of course, be isostructural, and mixed crystals could easily occur, giving the narrow range of stoichiometry observed in our experiments. We found no evidence for the production of  $WCl_3Br$  in our studies and, in view of the extreme sensitivity of the reaction to traces of moisture and oxygen, it seems likely that the earlier workers,<sup>1</sup> whose experiments we tried to verify, may also have inadvertently made  $WOCl_3Br$  rather than  $WCl_3Br$ .

#### EXPERIMENTAL

The starting material,  $K_3W_2Cl_9$ , prepared by the method of Young and his co-workers,<sup>4</sup> was purified by crystallization from saturated aqueous hydrochloric acid. The sample was washed with ethanol, ether, and dried *in vacuo*. The bromination was carried out by the method of Young and Laudise.<sup>1</sup>  $K_3W_2Cl_9$  (10 g.) was placed in a silica boat in a Pyrex glass tube. White-spot nitrogen (British Oxygen Company Limited) was passed over a B.T.S. deoxygenating catalyst, through a phosphoric oxide trap, and then over the sample for 1 hr. The sample was then heated to 450° and bromine was admitted with the nitrogen stream. A dark sublimate collected at the end of the heated section of the tube. On completion of the bromination reaction, this volatile product was sealed between two constrictions in the tube and transferred to a dry, oxygen-free glove-box. Resublimation of this product in an evacuated sealed tube with a 180–20° temperature gradient yielded a number of fractions, the most volatile of which was removed and analyzed. The small quantity of such samples precluded complete analysis in some cases, but the tungsten content for all such samples fell in the range 47.2–50.8%. The total halide content was determined for a considerable number of these samples, and in all cases the ratio of tungsten : total halogen was 1 : 4. Individual halide analyses were undertaken for the  $X$ -ray sample and found within experimental error to be consistent with the formula  $WOCl_3Br$  (e.g., Found: W, 47.7; Br, 21.6; Cl, 28.8.  $WOCl_3Br$  requires W, 47.7; Br, 20.7; Cl, 27.5%). The oxidation state of tungsten in this sample was determined as being +6. This sample was soluble in polar solvents only (cf.  $WOCl_4$ <sup>5</sup>). The  $X$ -ray powder diffraction patterns of several samples showed them to be isomorphous with  $WOCl_4$  and  $WOBr_4$ .

In two experiments the phases  $WCl_3Br_2$  and  $WCl_3Br_{2.4}$  were isolated from the fractional sublimation of the initial reaction products [(a) Found: W, 40.4; Br, 35.4; Cl, 23.9.  $WCl_3Br_2$  requires W, 40.8; Br, 35.6; Cl, 23.6%. (b) Found: W, 39.0%; W : halide ratio 1 : 5.4.  $WCl_3Br_{2.4}$

<sup>3</sup> R. V. Parish, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 315.

<sup>4</sup> R. A. Laudise and R. C. Young, *J. Amer. Chem. Soc.*, 1955, **77**, 5288.

<sup>5</sup> G. W. A. Fowles and J. L. Frost, *J. Chem. Soc. (A)*, 1967, 671.

requires W, 38.0%]). The room-temperature magnetic moment of  $\text{WCl}_3\text{Br}_2$  was found to be 1.15 B.M., and the compound was soluble in benzene as would be expected. No W-O bands appeared in its i.r. spectrum.

All reaction products were handled in an atmosphere of deoxygenated dry nitrogen. I.r. spectra were recorded as Nujol mulls between KBr or Polythene plates using Perkin-Elmer 125 and Grubb Parsons DM4 Mark II spectrometers. X-Ray data were obtained on single-crystal specimens (obtained by careful sublimation in a temperature gradient) using a Weissenberg camera and filtered Cu radiation, and on powder samples using a Debye-Scherrer camera and Co radiation.

Tungsten analyses were obtained both by precipitation as the oxinate and by hydrolysis and ignition to the oxide.

Total halide determinations were obtained by Volhard's titration, but co-precipitation of tungstic acid was found to interfere with gravimetric determination of halogen as silver halide. Consequently, individual halide analyses were obtained commercially by Dr. M. Beller of Göttingen. Oxidation states were determined by the ceric sulphate method which was found to be satisfactory for  $\text{K}_3\text{W}_2\text{Cl}_8$ . Bromide was found to have no significant effect on these titrations at the concentrations used. Magnetic-susceptibility measurements were made by the Faraday method.

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