Some New Thiohalides of Molybdenum and Tungsten

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Summary Synthetic methods are reported for four new thiohalides, $MoSCl_3$, $WSCl_3$, and WSX_4 (X=Cl,Br), whose physical properties indicate polymeric structures for the $MSCl_3$ compounds (with M–S–M bridging bonds), but the presence of terminal W=S bonds for WSX_4.

ALTHOUGH transition-metal oxyhalides are well established, relatively little is known of analogous thiohalides. The only information concerning such compounds is sparse on characterisation and structural detail. Thus $TiSCl_2$ is described[1] as a thermally unstable solid, and the molybdenum and tungsten compounds MS_2Cl_2 are reported,[2] but not characterised. The niobium compounds NbS_2X_2 (X=Cl,Br), which are better established,[3] contain S_2^{2-} units and Nb–Nb bonds rather than direct Nb–S bonds. We are making a comprehensive study of transition-metal thiohalides and their complexes and report the thiohalides $MoSCl_3$, $WSCl_3$, $WSCl_4$, and $WSBr_4$.

The compound $WSCl_4$ is obtained (70%) by the reaction of stoicheiometric quantities of WCl_6 and Sb_2S_3; the reaction is spontaneous and proceeds vigorously on gentle warming. $WSBr_4$ is prepared by the analogous reaction from WBr_6. The thiochloride is obtained also in 100% yield from the reaction of either WCl_6 or WCl_5 with elemental sulphur at 120°; even with an excess of sulphur, $WSCl_4$ is the only thiochloride formed. The reaction of Sb_2S_3 at 150° with the pentachlorides $MoCl_5$ and WCl_5 gives the thiohalides $MSCl_3$. Attempts to obtain $WSCl_3$ by reduction of $WSCl_4$ with aluminium (*cf.* analogous reduction of $WOCl_4$[4]) gives products contaminated with aluminium sulphide.

In moist air all the thiohalides are unstable and evolve H_2S and hydrogen halide. $WSCl_4$ (mp. 146°) sublimes readily under vacuum to yield diamagnetic dark ruby-red crystals; and dark green crystals of $WSBr_4$ are obtained at 180—200°. The trichlorides $MOSCl_3$ (greenish-black) and $WSCl_3$ (black) are involatile.

I.r. spectra (Table) show strong peaks at 569 cm^{-1} and 555 cm^{-1} for $WSCl_4$ and $WSBr_4$ respectively, which we assign to terminal W=S bonds. Peaks in the range 400—510 cm^{-1} are assigned[5] to metal–sulphur bonds for ionic transition metal–sulphur compounds. The absence of peaks above 383 cm^{-1} in the spectra of the $MSCl_3$ compounds indicate polymeric structures with M–S–M bridging bonds. Both the latter compounds are paramagnetic (Table), the low moments being similar to that found for $WOCl_3$ (μ = 0·50 B.M.);[4] these low values may be attributed to interactions of electrons on adjacent metal atoms through a non-linear M–S–M system.

Compound	μ (B.M.) at 293°	I.r. spectra (cm^{-1})
$WSCl_4$	0	569s, 392sh, 355s, 306s, 285w.
$WSBr_4$	0	555s, 395w, 346w, 250m.
$MoSCl_3$	0·75	383sh, 364m, 320m, 271w.
$WSCl_3$	0·54	373s, 334sh, 298w.

X-Ray powder data shows the $MSCl_3$ compounds to be isomorphous, although the patterns are quite different from those of the analogous oxychlorides.

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