Journal of the Less-Common Metals, 53 (1977) 291 - 293

Short Communication

Preparation and characterization of thiochlorides of vanadium(III), niobium(V), tantalum(V), molybdenum(V) and tungsten(VI)

AHMED O. BAGHLAF and ALAN THOMPSON

Department of Chemistry, University of Manchester, Manchester, M13 9PL (Gt. Britain)

(Received November 15, 1976)

Transition metal thiohalides WSX_4, MS_2X_2, MSX_3 (M = Mo, W; X = Cl, Br) and VSCl have previously been prepared by the reaction of Sb_2S_3 and the appropriate halide in a sealed tube [1, 2]. $WSCl_4$ and MoS_2Cl_2 have also been obtained by the action of elemental sulphur on WCl_6 and by the reaction of S_2X_2 with molybdenum metal [3, 4]. NbS_2Cl_2 has been prepared by the reaction of Nb metal [5] with S_2X_2; $TiSCl_2$ has been prepared by the action of hydrogen sulphide on $TiCl_4$ in CS_2 solution below 0 °C [6]. In this work a method of preparing $WSCl_4$ and $MSCl_3$ (M = Nb, Ta, Mo) has been developed [7] in which the appropriate chloride is reacted with boron sulphide. Since the completion of this work a brief report of an independent preparation of a series of thiohalides by the Sb_2S_3 route has appeared [8].

Experimental

Materials

$NbCl_5$, $TaCl_5$ (specified purity 99.9%), $MoCl_5$ (Koch-Light Ltd.) and B_2S_3 (Organic/Inorganic Chemical Corp.,) were used as supplied. WCl_6 (Koch-Light Ltd.) was purified by passing a stream of pure gaseous chlorine over the heated material [2].

The moisture-sensitive pentachlorides, tungsten hexachloride and the thiochlorides were handled in a dry nitrogen atmosphere in a glove-box; preparative reactions were carried out in sealed evacuated tubes. The organic solvents were usually dried by fractionation either from phosphorus pentoxide or from sodium metal.

Preparation

$WSCl_4$ was prepared by the reaction of WCl_6 (1.2996 g) with B_2S_3 (0.1287 g) at 100 - 120 °C and was purified by sublimation in a sealed tube at 140 °C. The other thiochlorides $MSCl_3$ (M = Nb, Ta, Mo) were prepared similarly by the reaction of stoichiometric amounts of MCl_5 and B_2S_3 at 90 °C (Nb), 80 °C (Ta) or 190 °C (Mo). Both $NbCl_5$ and $TaCl_5$ react with B_2S_3 at room temperature, as shown by the change in colour of the MCl_5 and the formation of liquid BCl_3 which was condensed in a side arm cooled by liquid nitrogen.

Analysis

Niobium, tantalum, molybdenum and tungsten were determined by atomic absorption spectroscopy. Chlorine was determined by potentiometric titration. The analytical results are summarised in Table 1.

TABLE 1

Compound	Colour	Analysis			
		Found (%)		Calculated (%)	
		M	Cl	M	Cl
$WSCl_4$	Deep red	51.1	39.5	51.4	39.6
$NbSCl_3$	Deep green	40.2	46.4	40.2	46.0
$TaSCl_3$	Bright green	56.7	33.3	56.6	33.3
$MoSCl_3$	Black	41.4	45.7	40.9	45.4

Physical measurements

Infrared spectra (4000 - 200 cm^{-1}) were recorded using a Perkin–Elmer grating spectrometer model 225 with caesium iodide plates. The solid samples were prepared as mulls in Nujol. Attempts were made to record the Raman spectra of powdered solids using a Cary 82 laser Raman spectrometer but all the thiochlorides reported here decomposed when exposed to the laser beam. X-ray powder photographs of finely powdered samples were obtained using a Debye–Scherrer camera and Cu K_α radiation. Magnetic susceptibilities were measured using the Gouy method. Electron spin resonance (ESR) spectra were recorded on a Varian V4502 ESR spectrometer using a Q band klystron source.

Results and discussion

The compounds $MSCl_3$ (M = Nb, Ta, Mo), unlike $WSCl_4$, are insoluble in the common organic solvents such as dichloromethane, carbon tetrachloride, carbon disulphide, diethyl ether or benzene. However, $NbSCl_3$, $TaSCl_3$ and $WSCl_4$ are soluble in methyl cyanide and are present in solution as $MSCl_3 \cdot 2CH_3CN$ (M = Nb, Ta) and $WSCl_4 \cdot CH_3CN$ [7]. All the thiohalides described here are sensitive to moisture.

From X-ray structural studies [9] it is known that the sulphur atom is strongly bonded to tungsten; the strong feature at 562 cm^{-1} in the IR spectrum of $WSCl_4$ has accordingly been assigned to the $\nu(W{=}S)$ stretching mode. In the IR spectra of $MSCl_3$ the features at 550 cm^{-1}, 457 cm^{-1} and 394 cm^{-1} can be assigned to the $\nu(Nb{=}S)$, $\nu(Ta{=}S)$ and $\nu(Mo{=}S)$ stretching vibrations, respectively.

X-ray powder diffraction photographs of $MSCl_3$ (M = Nb, Ta, Mo) suggest that these compounds are isostructural. Magnetic susceptibility measurements on $MoSCl_3$ indicate that it is paramagnetic with μ_{eff} = 1.4 BM and

the ESR spectrum suggests that the molybdenum has formally a d^1 electronic configuration.

Acknowledgments

We thank Professor K. W. Bagnall and Dr. F. E. Mabbs for invaluable discussions, Mr. M. A. Hart for the microanalyses (Nb, Ta, Mo, W, S and Cl) and the King Abdulaziz University of Jeddah (Saudi Arabia) for the award of a scholarship (to A.O.B.).

References

1 D. Britnell, G. W. A. Fowles and D. A. Rice, J. Chem. Soc., Dalton Trans., 20 (1974) 2191.
2 A. O. Baghlaf, M. Sc. Thesis, University of Manchester, England, 1972.
3 N. S. Fortunatov and N. I. Timoshchenko, Ukr. Khim. Zh. Russ. Edn., 35 (1969) 1207.
4 J. P. Rannou and M. Sergent, C. R. Acad. Sci., Ser. C, 277 (1973) 465.
5 H. Schaefer and W. Beckmann, Z. Anorg. Allg. Chem., 347 (1966) 225.
6 V. P. Ehrlich and W. Siebert, Z. Anorg. Allg. Chem., 301 (1959) 288.
7 A. O. Baghlaf, Ph. D. Thesis, University of Manchester, England, 1975.
8 G. W. A. Fowles, R. J. Hobson, D. A. Rice and K. J. Shanton, Chem. Commun., 14 (1976) 552.
9 M. G. B. Drew and R. Mandyczewsky, J. Chem. Soc. A, 17 (1970) 2815.