Low-temperature Syntheses of Vanadium(III) and Molybdenum(IV) Bromides by Halide Exchange†

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Halide-exchange reactions of VCl_4 or $MoCl_5$ with dry HBr at temperatures between *ca.* −50 and +20 °C afforded the corresponding bromides, VBr_3 or $MoBr_4$, in good yields, presumably *via* the formation of unstable higher-valent bromide intermediates which undergo spontaneous loss of bromine. In corresponding reactions with HI the exchange was incomplete and mixed halides were obtained. At room temperature the VCl_4–HI system gave VCl_3 in an almost quantitative yield. By reaction of $MoBr_4$ with tetrahydrofuran (thf) $[MoBr_3(thf)_3]$ was isolated and its crystal structure determined: orthorhombic, space group *Pbcn* (no. 60), $a = 8.812(2)$, $b = 13.882(5)$, $c = 14.279(3)$ Å, $Z = 4$, $R = 0.063$. The molecule has the usual meridional geometry, typical of other $[MoX_3(thf)_3]$ derivatives (X = Cl or I).

Recently we have shown that the heavier halides of titanium(IV), niobium(V) and tantalum(V), MX_n (M = Ti, $n = 4$;[1a] M = Nb or Ta, $n = 5$;[1b] X = Br or I), can conveniently be prepared by treating MCl_n with dry HX (X = Br or I) in heptane or halogenated hydrocarbons at room temperature or below, in a halide-exchange reaction, the driving force presumably originating from the formation of HCl [ΔG°_f (ref. 2) −22.77 (X = Cl), −12.73 (X = Br) or +0.38 kcal mol^{-1} (X = I)]. In the case of niobium(V), the Cl–Br exchange was also successfully carried out with Pr^{i}Br in a EtBr reaction medium.[1b]

The tendency of metal halides MX_n to undergo spontaneous loss of X_2 increases (*a*) in the order Cl < Br < I, (*b*) with increasing oxidation state of the metal and (*c*) at higher temperature. It was therefore thought that some intrinsically unstable species MX_n (X = Br or I) could be prepared at low temperature from the MCl_n–HX system or, alternatively, that the lower oxidation-state compounds MX_{n-1} could be obtained under relatively mild conditions, as an alternative to the conventional synthetic route where the elements are heated at high temperatures.[3]

Several papers have appeared concerning the thermal stability of VX_4.[4] Recently, VCl_4 has been found[5] to undergo reduction in solution to VCl_3 even at room temperature in the dark, while VBr_4 is known[6] to decompose to VBr_3 and Br_2 above −25 °C. Similarly, $MoBr_5$ is not thermally stable, giving $MoBr_4$ or $MoBr_3$ on moderate heating.[7] Only those iodide derivatives where the metal is in a low oxidation state have been satisfactorily characterized[8] (*e.g.*., VI_3, MoI_3 or MoI_2).

Here we report that excellent yields of VBr_3 or $MoBr_4$ can be obtained from the reaction of HBr with VCl_4 or $MoCl_5$, in heptane or EtBr respectively at low temperature. Some I–Cl exchange reactions, triggered by dry HI, are also presented together with the crystal structure of *mer*-$[MoBr_3(thf)_3]$ (thf = tetrahydrofuran).

Results and Discussion

The room-temperature reaction of VCl_4 with dry HBr in heptane is fast and gives a mixture of the virtually insoluble species VCl_3 and VCl_2Br. However, when a solution of VCl_4 in heptane was treated with HBr at *ca.* −35 °C, no precipitate was observed and instead a deep violet solution, presumably containing VBr_4,[6] was obtained. This solution was stable at low temperature but slowly evolved bromine on warming to room temperature to afford VBr_3 in excellent yield. The product was characterized by conventional methods and by its reaction with thf to give $[VBr_3(thf)_3]$[9] [equations (1) and (2)].

$$VCl_4 + 4HBr \xrightarrow{ca.\ -35\ ^\circ C} VBr_4 + 4HCl \xrightarrow{ca.\ 20\ ^\circ C} VBr_3 + \tfrac{1}{2}Br_2 \quad (1)$$

$$VBr_3 + 3thf \xrightarrow{thf} [VBr_3(thf)_3] \quad (2)$$

In the case of molybdenum, similar reactivity was observed. Thus treatment of an EtBr solution of $MoCl_5$ (*ca.* 5% w/w) with HBr at low temperature caused a drastic colour change followed by the separation of a black solid as the temperature was allowed to increase [equation (3)].

$$MoCl_5 \xrightarrow{HBr,\ ca.\ -50\ ^\circ C} MoBr_5 \xrightarrow{ca.\ 20\ ^\circ C} MoBr_4 + \tfrac{1}{2}Br_2 \quad (3)$$

The MCl_n–HI exchange reactions have also been studied. When a heptane solution of VCl_4 was exposed to dry HI at room temperature the almost instantaneous separation of VCl_3 was observed. This is believed to be due to the formation of a metastable VCl_3I intermediate undergoing loss of I_2 at a rate faster than the second halide exchange. Mixed metal halides were obtained in the MCl_n–HI systems at *ca.* −50 °C (M = V^{IV} or Mo^V).

These results are particularly relevant to the preparation of $MoBr_4$. Indeed molybdenum tetrahalides are difficult to prepare because of their tendency to disproportionate (MoF_4[10] and $MoCl_4$[11]) and to decompose (to $MoBr_3$ and Br_2 in the case of $MoBr_4$). It is therefore interesting to note that the reaction of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: cal ≈ 4.184 J, 1 mmHg ≈ 133 Pa.

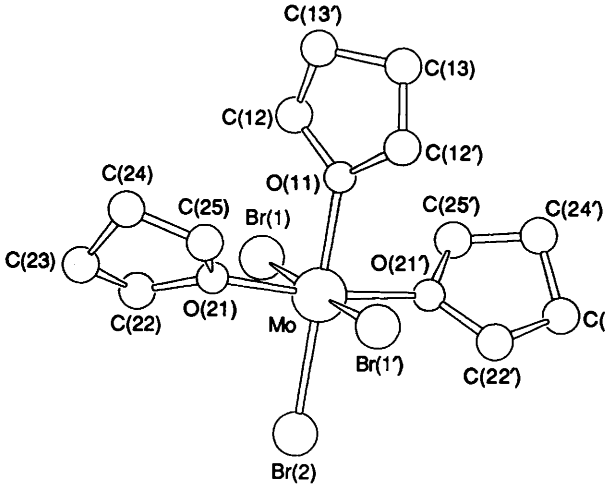

Fig. 1 A SCHAKAL[16] plot of the molecular structure of *mer*-[$MoBr_3(thf)_3$]

Table 1 Selected bond distances (Å) and angles (°) in *mer*-[$MoBr_3(thf)_3$]. Estimated standard deviations (e.s.d.s) in parentheses refer to the least significant digit

Mo–Br(1)	2.570(2)	Mo–O(11)	2.169(9)
Mo–Br(2)	2.534(2)	Mo–O(21)	2.120(7)
Br(1)–Mo–Br(2)	91.18(4)	O(11)–Mo–O(21)	85.7(2)
Br(1)–Mo–O(11)	88.82(4)	Br(1)–Mo–O(21)	90.1(2)
Br(2)–Mo–O(11)	180.0(1)	Br(2)–Mo–O(21)	94.3(2)

$MoCl_5$ with BBr_3 at 90–120 °C for 4 h afforded quantitative yields of $MoBr_3$[12] and that slightly impure $MoBr_4$ was obtained[13] from the reaction of $MoBr_3$ and Br_2 at 400 °C.

In an attempt to characterize the bromide derivative of molybdenum(IV) further, $MoBr_4$ was treated with acetonitrile to give the known derivative [$MoBr_4(MeCN)_2$].[14] However, upon treatment with thf an orange-red solution was obtained, which on cooling gave orange crystals of [$MoBr_3(thf)_3$]. Although a detailed study was not carried out we suggest that the reduction of Mo^{IV} to Mo^{III} is solvent induced. Indeed thf may react with Lewis acids such as metal halides undergoing ring opening resulting in the formation of polymers and/or alkyl halides.[15]

Crystals of [$MoBr_3(thf)_3$] were studied by X-ray crystallography. The structure consists of a meridional arrangement of three bromide ions and three thf groups co-ordinated to the octahedral molybdenum(III) (Fig. 1). The same structure was found for the chloride complexes [$TiCl_3(thf)_3$],[17] [$VCl_3(thf)_3$][18] and [$MoCl_3(thf)_3$][19] although they crystallize in the monoclinic space group $P2_1/c$ and are therefore not isotypical with [$MoBr_3(thf)_3$]. Cotton and Poli[20] have reported the structure of *mer*-[$MoI_3(thf)_3$], a compound which was obtained from the oxidation of molybdenum(0) or molybdenum(II) organometallic derivatives with iodine; the crystals are orthorhombic and have the same space group as [$MoBr_3(thf)_3$] (*Pbcn*).

The atoms Br(2), Mo and O(11) occupy a special position on a two-fold axis of the space group *Pbcn*, and therefore the compound has the point symmetry C_2. The inner $MoBr_3O_3$ core of the complex almost fulfils the higher C_{2v} symmetry.

The Mo–Br bond lengths (Table 1) [2.534(2) and 2.570(2) Å] are similar to the Mo–Cl bond distances [2.387(2) and 2.441(2) Å] in *mer*-[$MoCl_3(thf)_3$][19] given the difference (0.14 Å) in the ionic radii of bromide and chloride.[22] The same applies to the Mo–I distances[20] [2.746(2) and 2.790(1) Å] in *mer*-[$MoI_3(thf)_3$], the difference in chloride and iodide ionic radii being 0.35 Å.[21] The Mo–O distances of 2.120(7) and 2.169(9) Å are in the range observed in *mer*-[$MoCl_3(thf)_3$]; as in the chloro derivative, there is only a small deviation from the ideal octahedral co-ordination geometry, with Br–Mo–Br [91.18(4)°] and O–Mo–O [85.7(2)°] being slightly different from the expected value (90°). It is noteworthy that the unique Mo–O distance *trans* to Br is significantly longer than the other two. This is a common feature in other *mer*-[$MX_3(thf)_3$] complexes[18b] including the molybdenum(III) derivatives.[19,20] The X-ray data of all three halogeno complexes of molybdenum(III) show that the difference in Mo–O distance between axial and equatorial thf groups decreases in the order Cl > Br > I. In *mer*-[$MoI_3(thf)_3$] the Mo–O distances of the equatorial and axial ligands are essentially identical [2.212(12) and 2.193(8) Å]. Effects other than that of the *trans* influence are involved in this case.

Experimental

Unless otherwise stated, all operations were carried out in an atmosphere of argon. The reaction vessels were oven dried before use. Solvents were dried by conventional methods.

Hydrogen bromide and HI (Matheson) and VCl_4 (Staufer) were used as received. Molybdenum pentachloride (Aldrich) was sublimed *in vacuo* before use. Heptane solutions of VCl_4, stored for limited periods of time at *ca.* −30 °C, were analysed for their chloride content prior to use.

Preparation of VBr_3.—(*a*) *At low temperature.* A 0.26 mol dm^{-3} heptane solution of VCl_4 (100 cm^3, 26 mmol) was cooled to *ca.* −35 °C and connected to a vacuum line and to a cylinder of HBr. Upon the introduction of HBr the orange-brown solution turned bright violet instantly. The vacuum/HBr operation was repeated several times within 5 h. The suspension was then allowed to warm to room temperature and stirred for 15 h. During this period, a green-black solid precipitated which was filtered off, washed with heptane and dried *in vacuo* affording 7.46 g (99% yield) of VBr_3 (Found: Br, 82.8; V, 17.0. Calc. for Br_3V: Br, 82.5; V, 17.5%); μ_{eff} (20 °C): 2.60 (diamagnetic correction, -1.48×10^{-9} m^3 mol^{-1}), in agreement with the literature.[22]

The filtered red-orange solution was vigorously shaken with an excess of a 0.5 mol dm^{-3} aqueous solution of KI and the iodine was titrated with a standard solution of $Na_2S_2O_3$, thus showing the presence of 12.9 mmol of Br_2 corresponding to a Br_2 : V molar ratio of 1 : 2.

(*b*) *At room temperature.* When a 0.67 mol dm^{-3} heptane solution of VCl_4 (30 cm^3, 20.1 mmol), made up to 80 cm^3 with heptane, was treated with dry HBr at room temperature a bright violet solution was obtained and a solid separated. The vacuum/HBr operation was repeated five times within 2 h, giving a brown-black solid in a red-orange solution. The suspension was then stirred at room temperature for 48 h, filtered, and the solid washed with heptane (5 × 25 cm^3) and dried *in vacuo* at room temperature affording 3.69 g of a 80 : 20 mixture of VCl_2Br and VCl_3 (Found: Cl + Br, 73.7; V, 26.3. Calc. for $Br_{0.8}Cl_{2.2}$ V: Cl + Br, 73.6; V, 26.4%).

Using method (*a*) but with the stoichiometric amount of HBr (HBr : V molar ratio 4.02 : 1), a 89% yield of VBr_3 was obtained. An IR spectrum of the solution showed an absorption at 2740 cm^{-1} typical of dissolved HCl.[23]

Upon reaction with thf (3 h, reflux) VBr_3 gave a 70% yield of the known compound[9] [$VBr_3(thf)_3$] (Found: C, 28.3; H, 4.7; Br, 47.1. Calc. for $C_{12}H_{24}Br_3O_3V$: C, 28.4; H, 4.7; Br, 47.3%).

Reaction of VCl_4 *with* HI.—(*a*) *At room temperature.* By operating as described above, a 0.67 mol dm^{-3} heptane solution of VCl_4 (50 cm^3, 33.5 mmol) was treated with dry HI. The resulting violet suspension was stirred at room temperature for 15 h and filtered. The solid was washed with heptane (8 × 25 cm^3), and heated at 50 °C (0.05 mmHg) for 4 h affording 5.12 g

Table 2 Crystal data for *mer*-[$MoBr_3(thf)_3$]

Formula	$C_{12}H_{24}Br_3MoO_3$
M	551.9
Crystal size/mm	0.15 × 0.35 × 0.50
Crystal system	Orthorhombic
Space group	*Pbcn* (no. 60)
a/Å	8.812(2)
b/Å	13.882(5)
c/Å	14.279(3)
U/Å^3	1746.6
T/°C	−60
Z	4
F(000)	1068
D_c/g cm^{-3}	2.099
Radiation (λ/Å)	Mo-Kα (0.710 73)
μ/cm^{-1}	75.35
Scan type	ω–2θ
θ Range/°	3–32
hkl	0–13, 0–21, −20 to 20
Number of measured reflections	6635
Number of unique reflections	2937
Number of measured reflections with $I > 3\sigma(I)$	1804
Number of parameters	89
Absorption correction	DIFABS
Min, max, average correction	0.6028, 1.2258, 0.9849
Extinction coefficient	3.4501×10^{-8}
$R(\Sigma\|\Delta F\|/\Sigma\|F_o\|)$	0.063
$R'\{[\Sigma w(\Delta F)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}; w = 1/\sigma^2\|F_o\|\}$	0.067

Table 3 Atomic coordinates for *mer*-[$MoBr_3(thf)_3$] with e.s.d.s in parentheses

Atom	x	y	z
Mo	0.000	0.358 81(7)	0.250
Br(1)	0.185 4(1)	0.362 63(9)	0.111 07(7)
Br(2)	0.000	0.176 3(1)	0.250
O(11)	0.000	0.515 1(6)	0.250
O(21)	−0.185 4(8)	0.370 2(5)	0.156 1(4)
C(12)	0.023(2)	0.576 5(8)	0.167 2(9)
C(13)	0.019(2)	0.674 9(9)	0.303(1)
C(22)	−0.200(1)	0.330 6(9)	0.061 7(8)
C(23)	−0.352(1)	0.365(1)	0.023 1(8)
C(24)	−0.385(2)	0.455(1)	0.081 3(9)
C(25)	−0.321(1)	0.429 9(8)	0.176 0(7)

(97% yield) of VCl_3 (Found: Cl, 67.5; V, 32.4. Calc. for Cl_3V: Cl, 67.6; V, 32.4%).

(*b*) *At low temperature*. As in the preparation of VBr_3, a 0.52 mol dm^{-3} heptane solution of VCl_4 (50 cm^3, 26 mmol) was diluted with heptane and treated with HI at *ca.* −50 °C. A violet solid was obtained on mixing the reagents. The suspension was then allowed to warm to room temperature and stirred for 15 h. The resulting suspension was filtered and the violet-black solid was washed with heptane (10 × 25 cm^3) and heated at 50 °C (0.05 mmHg) for 4 h affording 7.93 g of *ca.* 1 : 1 mixture of VCl_2I and $VClI_2$ (Found: Cl + I, 82.6; V, 17.5. Calc. for $Cl_{1.5}I_{1.5}V$: Cl + I, 82.7; V, 17.3%).

Synthesis of $MoBr_4$.—A red-brown solution of $MoCl_5$ (2.02 g, 7.4 mmol) in EtBr (35 cm^3) was cooled to *ca.* −50 °C and connected to a vacuum line and to a cylinder of HBr. Precipitation of a solid was observed on the introduction of HBr and after 10 min the solution had turned colourless. The vacuum/HBr operation was repeated five times in 2 h. The suspension was then allowed to warm to room temperature and stirred for 15 h. The black solid was filtered off, washed with heptane (3 × 10 cm^3) and dried *in vacuo* affording 2.68 g (87% yield) of $MoBr_4$ (Found: Br, 76.7; Mo, 23.9. Calc. for Br_4Mo: Br, 76.9; Mo, 23.1%); μ_{eff} (20 °C): 1.24 (diamagnetic correction, -2.04×10^{-9} m^3 mol^{-1}), in agreement with the literature.[13]

The filtered red-orange solution was vigorously shaken with an excess of a 0.5 mol dm^{-3} aqueous solution of KI and the iodine was titrated with a standard solution of $Na_2S_2O_3$, thus showing the presence of 3.29 mmol of Br_2 corresponding to a Br_2 : Mo molar ratio of 0.445 : 1. Upon treatment with MeCN (3 h, room temperature), $MoBr_4$ gave a 70% yield of the known species[14] [$MoBr_4(MeCN)_2$].

Reaction of $MoBr_4$ *with thf*.—The compound $MoBr_4$ (0.311 g, 0.75 mmol) was added to cold (*ca.* −78 °C) thf (25 cm^3). No reaction took place at low temperature. The temperature was then raised to an ambient value and the formation of a red-orange solution was observed. After removal of *ca.* 10 cm^3 of thf, the solution was treated with heptane (30 cm^3) and cooled to *ca.* −30 °C. Orange crystals (0.245 g, 59% yield) of [$MoBr_3(thf)_3$][24] were obtained after several days.

X-Ray Crystal Structure of [$MoBr_3(thf)_3$].—A transparent, orange crystal of [$MoBr_3(thf)_3$] with approximate dimensions 0.15 × 0.35 × 0.50 mm was mounted on a glass rod in an Enraf–Nonius CAD4 single-crystal diffractometer (graphite monochromator) equipped with Mo-Kα radiation at *ca.* −60 °C. The lattice parameters (Table 2) of the orthorhombic crystal were refined using 25 reflections in the θ range 7.2–13.9°. The data collection with ω–2θ scans at −60 °C between θ = 3 and 32° resulted in 6635 reflections. Three reflections monitored every hour showed no loss of intensity (see Table 2).

The structure was solved using direct methods[25] and subsequent Fourier difference syntheses.[26] Isotropic refinement of the structural model including all non-hydrogen atoms converged to $R = 0.105$. An empirical absorption correction using the program DIFABS[27] and merging of 1804 data with $I > 3\sigma(I)$ improved the R value (0.089), which was reduced further to 0.063 after anisotropic refinements of all atoms. On applying the extinction coefficient[28] a final R' value of 0.067 was obtained. Atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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