Journal of the Less-Common Metals, *124* (1986) 135 - 139

SOME NEW COMPLEXES OF TRIBROMOOXIDE NIOBIUM(V)

K. BEHZADI, A. I. T. AHWAZ IRAN and A. THOMPSON

Department of Chemistry, University of Manchester, Manchester M13 9PL (U.K.)

(Received March 3, 1986)

Summary

New complexes of the type $NbOBr_3 \cdot 2L$ (where $L \equiv Ph_3PO$, MeCN, C_4H_8S) and $NbOBr_3 \cdot Et_2S$ have been prepared by the direct reaction of $NbOBr_3$ with ligands. $NbOBr_3 \cdot 2L$ (where $L \equiv Ph_3PO$, Me_2SO and $(Me_2N)_2CO$) have been prepared from $NbBr_5$ and an excess of ligand by an oxygen abstraction reaction.

1. Introduction

Transition metal oxohalides react with monodentate (L) and bidentate (B) ligands containing oxygen, sulphur and nitrogen as a donor atom to yield complexes of type $MOX_3 \cdot L$, $MOX_3 \cdot 2L$ and $MOX_3 \cdot B$.

The reactions of trihalooxoniobium(V) and tantalum(V) have received much less attention than the analogous molybdenum and tungsten compounds. However, $MOCl_3 \cdot 2MeCN$ (where $M \equiv Nb$, Ta) [1, 2], $NbOX_3 \cdot B$ (where $X \equiv Cl$, Br and $B \equiv$ 2,2′-bipyridyl and 1,10-phenanthroline) [3 - 5], $NbOCl_3 \cdot 2Me_2SO$ [6], $NbOCl_3 \cdot 2Ph_3PO$ and $NbOCl_3 \cdot 2(Me_2N)_3PO$ [7, 8], have been reported by the direct reaction of $NbOX_3$ with ligands. The reaction of niobium pentachloride with dimethyl- and diphenylsulphoxide demonstrates the ability of niobium(V) chloride to abstract oxygen from sulphoxides with formation of chlorooxo complexes of the type $NbOCl_3 \cdot 2L$ [6]. In the same manner Ph_3PO and Ph_3AsO undergo oxygen abstraction with niobium, tantalum pentachloride and $TaBr_5$ [9, 10].

Now we report the preparation of a number of complexes having general formulae of $NbOBr_3 \cdot 2L$ (where $L \equiv Ph_3PO$, MeCN, C_4H_8S, Me_2SO and $(Me_2N)_2CO$) and $NbOBr_3 \cdot Et_2S$.

2. Experimental details

The complexes were prepared and handled in a dry box filled with oxygen free dinitrogen.

0022-5088/86/$3.50

2.1. Materials

$NbBr_5$ (Alfa), Ph_3PO (BDH), Me_2SO (BDH), Et_2S (Ralph N. Emanuel), C_4H_8S (CDH), MeCN (Hopkin and Williams) were purified and dried by standard methods.

2.2. Analytical determination

Analyses of niobium, bromine, sulphur, carbon, hydrogen and nitrogen were carried out in the Microanalytical Laboratory of the Department of Chemistry, University of Manchester, by Mr. M. Hart.

2.3. Preparation of compounds

2.3.1. Preparation of $NbOBr_3$

$NbOBr_3$ was prepared by the reaction of niobium pentabromide with antimony trioxide in carbon disulphide in a dinitrogen atmosphere. $NbOBr_3$ requires Nb, 26.64%; Br, 68.76%. Analysis found Nb, 26.2%; Br, 67.8%.

2.3.2. Preparation of $NbOBr_3 \cdot 2Ph_3PO$

$NbOBr_3 \cdot 2Ph_3PO$ was prepared by the following routes:

(a) by the reaction of a dark red acetonitrile solution of $NbBr_5$ with the stoichiometric amount (1:3 mol ratio) of triphenylphosphine oxide which results in organge-yellow crystals;

(b) by the reaction of an acetonitrile solution of $NbOBr_3$ with a two-fold excess of triphenylphosphine oxide which results in the formation of an orange-yellow precipitate of the complex.

$NbOBr_3 \cdot 2Ph_3PO$ requires Nb, 10.7%; Br 26.52%; C, 47.73%; H, 3.31; P, 6.85%. Analysis found Nb, 10.1%; Br, 26.1%; C, 48.9%; H, 3.4%; P, 7.5%.

2.3.3. Preparation of $NbOBr_3 \cdot 2Me_2SO$

$NbOBr_3 \cdot 2Me_2SO$ was prepared by the direct reaction of dark-red acetonitrile solution of $NbBr_5$ with the stoichiometric amount (1:3 mol ratio) of dimethylsulphoxide, which results in the formation of an orange precipitate of the complex. $NbOBr_3 \cdot 2Me_2SO$ requires Nb, 18.41%; Br, 47.52%; C, 9.5%; H, 2.3%; S, 12.67%. Analysis found: Nb, 16.9%; Br, 48.2%; C, 9.8%; H, 2.2%; S, 14.2%.

2.3.4. Preparation of $NbOBr_3 \cdot 2(Me_2N)_2CO$

$NbOBr_3 \cdot 2(Me_2N)_2CO$ was prepared by the direct reaction of a suspension of $NbOBr_3$ in dichloromethane with a two-fold excess of ligand which results in the formation of a pale yellow precipitate. $NbOBr_3 \cdot 2(Me_2N)_2CO$ requires Nb, 16.00%; Br, 41.3%; C, 20.65%; H, 4.13%; N, 9.64%. Analysis found: Nb, 15.3%; Br, 39.4%; C, 22.1%; H, 4.6%; N, 10.1%.

2.3.5. Preparation of $NbOBr_3 \cdot 2C_4H_8S$

$NbOBr_3 \cdot 2C_4H_8S$ was prepared by the reaction of $NbOBr_3$ with a large excess of ligand. Removal of excess C_4H_8S results in an orange precipitate of the complex. $NbOBr_3 \cdot 2C_4H_8S$ requires Nb, 17.71%; Br, 45.71%; C, 18.28%;

H, 3.04%; S, 12.1%. Analysis found: Nb, 18.2%; Br, 44.2%; C, 18.28%; H, 3.05%; S, 9.6%.

2.3.6. *Preparation of $NbOBr_3 \cdot Et_2S$*

The procedure was similar to that used in the preparation of $NbOBr_3 \cdot 2C_4H_8S$. $NbOBr_3 \cdot Et_2S$ requires Nb, 21.18%; Br, 54.66%; C, 10.93%; H, 2.27%; S, 7.29%; Analysis found: Nb, 21.3%; Br, 52.2%; C, 11.3%; H, 2.6%; S, 7.8%.

2.3.7. *Preparation of $NbOBr_3 \cdot 2MeCN$*

The procedure was similar to that used in the preparation of $NbOBr_3 \cdot Et_2S$. $NbOBr_3 \cdot 2MeCN$ requires Nb, 23.89%; Br, 61.53%; C, 6.15%; H, 0.76%; N, 3.94%. Analysis found: Nb, 24.0%; Br, 57.4%; C, 6.8%; H, 0.9%; N, 4.0%.

2.4. *Physical measurements*

2.4.1. *IR spectra*

IR spectra were recorded using Perkin–Elmer model 257 (4000 - 625 cm^{-1}) and Perkin–Elmer model 225 (625 - 200 cm^{-1}) instruments. Nujol mulls were prepared in the dry box.

2.4.2. *Raman spectra*

Raman spectra of the powdered samples were recorded using a Cary 82 laser Raman spectrometer.

2.4.3. *X-Ray powder photographs*

Photographs were obtained using a Debye–Scherrer camera with a diameter of 5.37 cm. In all cases Cu Kα radiation was used.

3. Results and discussion

The compounds $NbOBr_3 \cdot 2L$ (where L ≡ Ph_3PO, Me_2SO, MeCN, C_4H_8S) and $NbOBr_3 \cdot Et_2S$ are soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, MeCN, CCl_4 and CS_2. All compounds are coloured in the range yellowish-orange to reddish-orange and are highly moisture sensitive.

Triphenylphosphine oxide and dimethylsulphoxide undergo an oxygen abstraction reaction with $NbBr_5$ to form tribromooxide niobium(V) complexes of $NbOBr_3 \cdot 2Ph_3PO$ and $NbOBr_3 \cdot 2Me_2SO$ respectively.

Recently the crystal structure of $NbOCl_3 \cdot 2Ph_3PO$ has been reported [17] to be in the monoclinic system with space group $C2/c$ and lattice dimensions of $a = 14.029(3)$, $b = 13.124(2)$, $c = 19.330(5)$ Å.

The recorded IR and Raman spectra of $NbOBr_3 \cdot 2Ph_3PO$ show strong absorptions at 938 cm^{-1} which are assigned to the ν(Nb=O) stretching vibration. The X-ray powder diffraction data of $NbOCl_3 \cdot 2Ph_3PO$, $NbOBr_3 \cdot 2Ph_3PO$ and $MoOCl_3 \cdot 2Ph_3PO$ showed that all these complexes are isostructural and $NbOBr_2 \cdot 2Ph_3PO$ has two molecules of ligand in *cis* positions [12, 13]. This is supported by the crystal structure of $NbOCl_3 \cdot 2Ph_3PO$ [17].

$NbOCl_3 \cdot POCl_3$ has been shown unequivocally to contain an oxygen bridged tetrametric unit [14, 15]. Direct alkoxylation of trichlorooxide niobium(V) resulted in the formation of niobium oxoalkoxide derivatives. The molecular constitution of the solution of these compounds in nonpolar solvent has been interpreted as a dynamic equilibrium between various μ-alkoxide and μ-oxo-dimeric units. The presence of alkoxide was confirmed by the IR absorption in the range 770 - 720 cm^{-1} which has been assigned to the μ-oxo stretching absorption for $NbOCl_2(OMe) \cdot MeOH$ [16].

The recorded IR spectra of $NbOBr_3 \cdot 2Me_2SO$, $NbOBr_3 \cdot 2C_4H_8S$, $NbOBr_3 \cdot 2MeCN$ and $NbOBr_3 \cdot Et_2S$ showed strong broad absorption at 790 - 735, 799 - 721, 794 - 720 and 800 - 722 cm^{-1} respectively which may be assigned to a Nb—O—Nb stretching vibration.

$NbOCl_3 \cdot 2MeCN$ crystallizes in the space group $P\bar{1}$ with $Z = 2$ and both MeCN are non-equivalent since the Nb—N bond lengths are 2.245(9) and 2.44(2) Å [17]. The two strong absorptions of free MeCN at 2291 and 2250 cm^{-1}, which are assigned to a combination of symmetric CH_3 deformation and C—C stretching, and C≡N stretching vibrations respectively [18], have shifted upon coordination to higher frequencies at 2308 and 2280 cm^{-1} for $NbOBr_3 \cdot 2MeCN$. In $NbOCl_3 \cdot 2MeCN$, since both MeCN are not equivalent, these modes are shifted to 2308, 2282 and 2297, 2272 cm^{-1} [17].

The assignment of the C—S frequency in Et_2S is complicated and the frequencies associated with the C—S stretching vibration have been assigned at 640, 660, 693, 746 and 781 cm^{-1} [19]. The absorptions at 722 and 630 cm^{-1} for $NbOBr_3 \cdot Et_2S$ are probably due to C—S stretching modes but it is difficult to say which modes these are, or what changes have occurred on coordination.

The reaction of tetrahydrothiophene with tribromosulphide niobium(V) results in the formation of a series thiobromide complexes, one of which is $NbSBr_3 \cdot 2C_4H_8S$. The crystal structure of $NbSBr_3 \cdot 2C_4H_8S$ is monoclinic with space group of $P21/n$; in this complex the metal is six-coordinate being bonded to terminal sulphur, three bromine atoms and two molecules of ligand through the sulphur atom; one of the ligands is *trans* to the Nb=S bond [20].

The band at 683 cm^{-1} in the IR spectrum of liquid tetrahydrothiophene has been assigned to a symmetric stretching frequency, involving both ring and C—S bonds [21]. In the recorded spectrum of C_4H_8S the strong absorption at 687 cm^{-1} has been assigned to the frequencies associated with the C—S stretching vibration which on complex formation is shifted to 670 cm^{-1} in the spectrum of $NbOBr_3 \cdot 2C_4H_8S$.

The lowering of the ν(S=O) frequency of dimethylsulphoxide on coordination through sulphoxide oxygen has been discussed [22]. Fairbrother and coworkers [6] have reported the ν(S=O) stretching vibration of $NbOCl_3 \cdot 2Me_2SO$ and $NbOCl_3 \cdot 2Ph_2SO$ occurred at (915, 930) and 940 cm^{-1} respectively. The absorption at 973 cm^{-1} in the IR spectrum of $NbOBr_3 \cdot 2Me_2SO$ is assigned to the ν(S=O) stretching vibration.

The IR spectrum of $(Me_2N)_2CO$ shows a strong broad band at 1660 - 1645 cm^{-1} which is assigned to the $\nu(C{=}O)$ stretching vibration and strong absorption at 1500 cm^{-1} corresponding to the NCN antisymmetric vibration [23]. The IR spectrum of $NbOBr_3 \cdot 2(Me_2N)_2CO$ showed strong absorptions at 1750, 1580, 1530 and 1450 cm^{-1}. If the absorptions at 1580 and 1530 cm^{-1} are assigned to $\nu(C{=}O)$ and NCN antisymmetric vibrations respectively, it is difficult to assign the vibration at 1750 cm^{-1}. Another possibility is that coordination is through nitrogen and this should result in the $\nu(C{=}O)$ and NCN antisymmetric vibrations being moved to higher and lower frequencies respectively. Therefore the absorptions at 1750 and 1450 cm^{-1} may be assigned to $\nu(C{=}O)$ and NCN antisymmetric vibrations respectively. Therefore from this evidence it is not possible to be conclusive about the mode of coordination of $(Me_2N)_2CO$ to $NbOBr_3$.

The IR spectra of $NbOBr_3 \cdot 2Ph_3PO$, $NbOBr_3 \cdot 2Me_2SO$, $NbOBr_3 \cdot 2C_4H_8S$, $NbOBr_3 \cdot 2MeCN$ and $NbOBr_3 \cdot Et_2S$ showed strong absorptions at (240, 236), 248, (258, 249) and 252 cm^{-1} respectively which are assigned to (Nb—Br) stretching vibrations.

References

1 J. G. Reiss, R. C. Muller and M. Postal, *Inorg. Chem., 13* (1974) 1302.
2 H. Boehland and F. M. Schnieder, *Z. Anorg. Allg. Chem., 269* (1958) 36.
3 C. Djordjevic and V. Katovic, *Chem. Commun.,* (1966) 224.
4 V. Katovic and C. Djodjevic, *Inorg. Chem., 9* (1970) 1720.
5 N. Brnicevic and C. Djordjevic, *J. Less-Common Met., 13* (1967) 470.
6 D. B. Copley, F. Fairbrother, K. H. Grundy and A. Thompson, *J. Less-Common Met., 6* (1964) 407.
7 R. J. Dorachnor, *J. Inorg. Nucl. Chem., 34* (1972) 2665.
8 A. O. Baghlaf, K. Behzadi and A. Thompson, *J. Less-Common Met., 57* (1) (1978) 103.
9 D. B. Copley, F. Fairbrother and A. Thompson, *J. Less-Common Met., 8* (1968) 256.
10 D. Brown, J. E. Easey and J. dePreez, *J. Chem. Soc. A,* (1966) 258.
11 V. S. Sergienk, *Koord. Khim., 10* (8) (1984) 1161.
12 F. E. Mabbs, personal communication, 1977.
13 K. Behzadi, *Ph.D. Thesis,* Manchester University, 1977.
14 M. G. Drew and R. J. Hobson, *Inorg. Chim. Acta, 72* (1983) 233.
15 G. Munnighoff, E. Hellner, M. El Essawi and K. Dehnicke, *Z. Kristallogr., 147* (1978) 231.
16 L. G. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chim. Acta, 41* (1980) 111.
17 C. Chavant, J. C. Daran, Y. Jeannin, G. Constant and R. Moroncho, *Acta Crystallogr., B, 31* (1983) 1828.
18 P. Venkateswarly, *J. Chem. Phys., 19* (1965) 293.
19 D. W. Scott, H. L. Fink, W. N. Hubbard, J. P. McCullough, C. D. Oliver, M. E. Gross, C. Katz, K. W. Williamson, G. Waddington and H. M. Huffman, *J. Am. Chem. Soc., 74* (1952) 4650.
20 M. G. B. Drew, R. D. A. Rice and D. A. Williams, *J. Chem. Soc., Dalton Trans.,* (1983) 2251.
21 R. L. Richards, *Ph.D. Thesis,* Manchester University, 1964.
22 F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem., 64* (1960) 1534.
23 H. L. Spelland and J. Laane, *Spectrochim. Acta., Part A, 28* (1972) 295.