447. *Reactions of Niobium*(V) *and Tantalum*(V) *Chlorides and Bromides with Some Cyclic Ethers and Thioethers*

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The reactions of the halides MX_5 (M = Nb or Ta; X = Cl or Br) with several cyclic ethers and thioethers have been shown to give 1 : 1 adducts. Spectral values for the thioxan complexes MX_5,C_4H_8OS have been interpreted as showing that the ligand co-ordinates through sulphur and not oxygen.

Elements of the titanium, vanadium, and chromium sub-groups are usually considered to act as class A acceptors [1] in their higher oxidation states and to bond to donors of the first row of the Periodic Table (*e.g.*, nitrogen and oxygen) rather than donors of subsequent rows (*e.g.*, phosphorus and sulphur). Investigations in this laboratory [2] have shown that with quadrivalent titanium, well defined complexes of the type $TiX_4,2L$ are formed by the chloride and bromide with a range of monodentate sulphur ligands; complexes TiX_4,B are formed with bidentate sulphur ligands. Furthermore, it has been shown [3] by infrared and nuclear magnetic resonance spectra that thioxan bonds to titanium through sulphur rather than through oxygen. This work has now been extended to the chlorides and bromides of niobium(V) and tantalum(V). It supplements studies previously reported by Fairbrother and his co-workers,[4,5] who found that these halides formed 1 : 1 adducts with dialkyl sulphides and with diethyl ether; they also reported that tetrahydrothiophen formed 2 : 1 adducts with the halides, and that these adducts were insoluble in excess of the ligand.

We have studied the reactions of the four halides (NbX_5 and TaX_5, where X = Cl and Br) with tetrahydrothiophen, pentamethylenesulphide, pentamethyleneoxide, 1,4-dioxan, and 1,4-thioxan. In every case, the halide dissolved in excess of ligand (the bromides being less soluble than the chlorides), and crystalline diamagnetic complexes were isolated by removal of excess of the ligand. Analysis of the complexes (cf. Table 1) showed them to be 1 : 1 adducts, except those formed in the pentamethylene oxide reactions, where polymerisation of the ligand also took place. This polymerisation is not unexpected, since tetrahydrofuran is also polymerised by these halides.[6] We were unable to isolate the insoluble $MX_5,2C_4H_8S$ complexes previously reported.[5]

The molecular weights of three of the compounds ($NbCl_5,C_4H_8O_2$, $NbCl_5,C_4H_8OS$, and $TaCl_5,C_4H_8O_2$), which were formed by potentially bidentate ligands, were measured ebullioscopically in benzene solution and found to correspond closely to monomeric values. Thus, in these complexes, the metal is either 6-co-ordinate or 7-co-ordinate, depending upon whether one or both of the donor atoms in the ligand bond to the metal; the latter possibility is unlikely, but has been suggested for $TiBr_4$,dioxan on the basis of infrared figures.[7]

Infrared and nuclear magnetic resonance spectra of the complexes have been measured in an attempt to check whether dioxan and thioxan are bonding through one or both of their donor atoms. The infrared spectra of the thioxan complexes suggest that there is no bonding through the oxygen atom, since the peak found at 1100 cm.$^{-1}$, (the asymmetric C–O–C stretching vibration), is not modified when the ligand co-ordinates. Although the inference is that thioxan bonds through sulphur, the infrared spectra cannot confirm this, because the C–S–C vibration is very weak and its peak position somewhat uncertain. The nuclear magnetic resonance spectrum does, however, provide strong support for this

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[1] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.
[2] K. L. Baker and G. W. A. Fowles, *J. Less-Common Metals*, 1965, **8**, 36.
[3] G. W. A. Fowles and R. A. Walton, *J.*, 1964, 4953.
[4] A. Cowley, F. Fairbrother, and N. Scott, *J.*, 1958, 3133.
[5] F. Fairbrother and J. F. Nixon, *J.*, 1962, 150.
[6] A. Cowley, Ph.D. Thesis, Manchester, 1956.
[7] R. H. Rolsten and H. H. Sisler, *J. Amer. Chem. Soc.*, 1957, **79**, 1068, 1819.

hypothesis. Thioxan itself shows a typical spectrum for an A_2B_2 system, with two asymmetric triplets. As a first approximation, we may attribute the first triplet to the protons on the carbon atoms adjacent to oxygen, and the second to the protons on the carbon atoms next to sulphur. When thioxan co-ordinates to the niobium(V) chloride, both triplets shift down field, but the " sulphur triplet " shifts almost twice as much as the " oxygen triplet," and becomes resolved further, giving a smaller additional peak between each of the main peaks. We accordingly suggest that in the thioxan complexes, bonding to the metal is through sulphur only.

The metal-sulphur bonds cannot be strengthened through d_π–d_π bonding, because the metals have no available *d* electrons, but there is a possibility of delocalisation of the halogen *p* electrons through the metal on to sulphur (cf. the boron complex[8] $B_2Cl_4,2SMe_2$). Measurements of ultraviolet spectra on solutions of the titanium complexes have, however, been interpreted[2] as showing that such delocalisation does not occur to any significant extent. The reason for bonds being formed by sulphur rather than by oxygen is attributed to the more ready polarisation of the sulphur lone pairs by the metals in a formally high oxidation state. It may be significant that with titanium[9] lowering of the oxidation state leads to much weaker titanium-sulphur bonds.

The infrared spectra of the dioxan adducts indicate that only one oxygen atom is bonded to the metal. Thus, the asymmetric C–O–C stretching frequency, which is found at 1125 cm.$^{-1}$ in the free ligand, is found unmodified in the complex, together with an additional peak of approximately the same intensity at 50—100 cm.$^{-1}$ lower frequency. Only $NbCl_5,C_4H_8O_2$ was sufficiently soluble in chloroform for a good nuclear magnetic resonance spectrum to be obtained, and this showed a single peak at 5·63 τ. This result is somewhat surprising, because splitting would have been expected, irrespective of whether the ligand co-ordinates through one or both of the oxygen atoms. The shift down-field of 0·67 τ confirms the presence of the co-ordinated ligand and the single peak shows all the protons to be equivalent. While it is possible that the chemical shifts coincide, it seems much more likely that in solution there is very rapid interchange of the ligand (from the labile complex) with a small amount of free ligand in solution; the required amount of free ligand would be very much less than could be detected in the molecular weight measurements.

The complexes formed by the metal halides with the cyclic ethers and thioethers containing only one donor atom appear to be straightforward 1 : 1 adducts, analogous to the alkyl cyanide complexes, MX_5,RCN, which were shown to contain 6-co-ordinate niobium and tantalum.[10] The infrared spectra show bands expected for the ligands themselves.

We have found no evidence, either analytical or infrared, for abstraction of oxygen or sulphur from the ligands, although the pentahalides are known to abstract oxygen from dialkyl and diaryl-sulphoxides giving niobium(V) and tantalum(V) oxotrichloride complexes of the type $MOX_3,2R_2SO$.[11]

EXPERIMENTAL

The niobium(V) and tantalum(V) halides were prepared from the powdered metals as described previously.[12] The ligands were dried by repeated distillation *in vacuo* from calcium hydride; the ethers were finally treated with potassium metal (thin film), and the thioethers with niobium(V) chloride.

Reactions.—Reactions were carried out in sealed ampoules with excess of ligand and in some cases (cf. Table 1) benzene in three-fold excess as diluent. After a suitable reaction period (usually several hours), the ampoule was opened and all volatiles were pumped off. Since all

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[8] T. Wartik and E. F. Apple, *J. Amer. Chem. Soc.*, 1958, **80**, 6155.

[9] K. L. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 1964, 362.

[10] K. Feenan and G. W. A. Fowles, *J.*, 1964, 2842.

[11] D. B. Copley, F. Fairbrother, K. H. Grundy, and A. Thompson, *J. Less-Common Metals*, 1964, **6**, 407.

[12] P. J. H. Carnell and G. W. A. Fowles, *J.*, 1959, 4113; *J. Less-Common Metals*, 1962, **4**, 40.

the complexes were very sensitive to moisture, handling was carried out in a vacuum system. Table 1 lists the products obtained.

Analysis.—Niobium and tantalum were determined by dissolving the complexes in anhydrous ethanol, precipitating the hydrated oxide with ammonium hydroxide, and igniting the precipitate to constant weight. Chlorine and bromine were determined by the Volhard method. Because the compounds were so very susceptible to hydrolysis, the analysis was difficult and tended to give rather low values for halogen and high values for metal; the carbon and hydrogen determinations were carried out by a professional analyst, and the high values obtained for hydrogen can be attributed to hydrolysis when the sample was weighed.

TABLE 1

Complexes formed by MX_5 (M = Nb or Ta; X = Cl or Br) with ethers and thioethers

	Found (%)					Calc. (%)						Mol. wt.	
Compound	C	H	X	M	S	C	H	X	M	S	Colour	Found	Calc.*
$NbCl_5,C_4H_8O_2$	13·7	2·2	48·0	25·4	—	13·4	2·3	49·5	25·9	—	Yellow	346	358
$NbCl_5,C_5H_{10}O$	—	—	46·7	24·7	—	—	—	49·8	26·1	—	Yellow	—	—
$NbCl_5,C_4H_8OS$ †	13·1	2·7	46·7	23·6	—	12·8	2·2	47·4	24·8	—	Orange	388	374
$NbCl_5,C_5H_{10}S$ †	16·6	3·0	46·0	23·1	7·9	16·1	2·7	47·6	24·9	8·6	Orange	—	—
$NbCl_5,C_4H_8S$ †	13·6	3·3	47·7	25·2	—	13·4	2·3	49·5	25·9	—	Orange	—	—
$NbBr_5,C_4H_8O_2$	9·2	2·2	67·1	17·1	—	8·3	1·4	68·8	16·0	—	D. red	—	—
$NbBr_5,C_4H_8OS$ †	8·6	2·2	65·7	14·8	—	8·1	1·4	67·0	15·6	—	D. red	—	—
$NbBr_5,C_5H_{10}S$ †	11·1	2·0	67·7	15·6	—	10·1	1·7	67·2	15·6	—	D. red	—	—
$NbBr_5,C_4H_8S$ †	9·6	2·6	65·7	16·3	5·1	8·3	1·4	68·8	16·0	5·5	D. red	—	—
$TaCl_5,C_4H_8O_2$	10·6	1·9	38·4	41·0	—	10·8	1·8	39·7	40·5	—	White	535	446
$TaCl_5,C_5H_{10}O$	—	—	37·1	40·1	—	—	—	39·9	40·7	—	White	—	—
$TaCl_5,C_4H_8OS$ †	10·3	1·9	38·9	39·7	6·2	10·4	1·7	38·5	39·3	6·9	Yellow	—	—
$TaCl_5,C_5H_{10}S$ †	13·6	2·2	37·9	39·1	6·3	13·0	2·2	38·5	39·3	7·0	P. yellow	—	—
$TaCl_5,C_4H_8S$ †	12·2	2·3	39·4	41·1	—	10·8	1·8	39·7	40·5	—	Yellow	—	—
$TaBr_5,C_4H_8O_2$	7·0	1·6	60·4	28·7	—	7·2	1·2	59·8	27·1	—	Yellow	—	—
$TaBr_5,C_4H_8OS$ †	7·9	1·8	57·2	27·2	—	7·0	1·2	58·3	26·4	—	Yellow	—	—
$TaBr_5,C_5H_{10}S$ †	8·9	1·6	58·0	28·0	4·4	8·8	1·5	58·5	26·5	4·7	Yellow	—	—
$TaBr_5,C_4H_8S$ †	7·7	2·0	60·4	29·3	4·9	7·2	1·2	59·8	27·1	4·8	Yellow	—	—

* Calculated values are for monomeric species. † Benzene as diluent.

TABLE 2

Nuclear magnetic resonance values for complexes of niobium(v) and tantalum(v) with ethers and thioethers

Complex	τ values		Complex	τ values	
Dioxan	6·30		$NbCl_5$, thioxan	5·72	6·72
Dithian		7·11	$NbCl_5$, dioxan	5·63	
Thioxan	6·15	7·43			

Physical Measurements.—Infrared spectra were measured on Nujol mulls with a Unicam S.P. 200 spectrophotometer, the usual precautions being taken against the presence of moisture. Molecular weight determinations were made ebullioscopically on benzene solutions by means of a modified form of the Gallenkamp ebulliometer. Nuclear magnetic resonance spectra were measured on chloroform solutions by means of a Varian A60 instrument; the results are shown in Table 2.

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