Reactions of Vanadium(V) Oxide Tribromide: Preparation and Properties of Vanadium(IV) Oxide Dibromide Complexes

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The reactions of $VOBr_3$ with a variety of ligands are reported. The following complexes have been prepared, and their structure studied: $VOBr_2(L-L)$ (where L–L = 1,2-dimethoxyethane or 2,2′-bipyridyl), $VOBr_2L_2$ (where L = tetrahydrofuran, 1,4-dioxan, hexamethylphosphoramide, pyridine, quinoline, triphenylphosphine, 1,4-thioxan, and tetrahydrothiophen), $VOBr_2L_3$ (where L = diphenyl sulphoxide or pyridine), and $VOBr_2L_5$ (where L = dimethyl sulphoxide).

UNTIL recently, the chemistry of vanadium(V) oxide tribromide had been very little studied.[1] We have studied the reactions of $VOBr_3$ with many common oxygen-, nitrogen-, sulphur-, and phosphorus-donor ligands, and in every case (with the possible exception of 2,2′-bipyridyl), reduction to vanadium(IV) immediately occurred, giving adducts of the form $VOBr_2L_x$. Only a few adducts of $VOBr_2$ are known,[2] and this work forms their first systematic study. Analysis of their far-i.r. spectra suggested a criterion for deducing their structure (*N.B.* there is a dearth of far-i.r. data on $VOCl_2$ complexes).

RESULTS AND DISCUSSION

Most of the reactions between $VOBr_3$ and ligands described in the Experimental section were initially carried out in a variety of solvents (*e.g.*, tetrahydrofuran, n-hexane, and 1,2-dichloroethane), but in all cases vanadium(IV) complexes having non-stoicheiometric V : Br ratios of greater than 1 : 2 were obtained. In these solvents the reactions proceeded with the liberation of bromine when stoicheiometric (1 : 2) ratios of $VOBr_3$ to ligand were used. We therefore chose cyclohexene as solvent (because of its reactivity towards free bromine) and were able to isolate pure stoicheiometric complexes for nitrogen-, oxygen-, and sulphur-donor ligands, but the reaction conditions (*e.g.*, relative concentrations, time of reaction, and washing procedure) were very critical. However, with triphenylphosphine, the reaction products were heavily contaminated with PPh_3Br_2. This was not unexpected as previous attempts to prepare triphenylphosphine complexes of vanadium(IV) have proved unsuccessful [3-5] [apart from a doubtful report of $VOCl_2(PPh_3)_2,H_2O$, which was supposedly prepared under *anhydrous* conditions [6]], the original report of $VOCl_2(PPh_3)_2,2H_2O$ [7] having been discredited.[4,8] We have succeeded in preparing $VOBr_2(PPh_3)_2$ by a ligand substitution reaction. Attempts to prepare complexes with ligands containing N–H bonds (*e.g.*, piperidine and 3,5-dimethylpyrazole) yielded complexes heavily contaminated with hydrobromide, formed during solvolysis and reduction of $VOBr_3$.

I.r. spectra (units of cm^{-1})

	ν(V=O)	ν(V–Br)	ν(L=O) [L = S or P] [c]	ν_{as}(C–O–C) [c]	ν_{sym}(C–O–C)	ν_{as}(C–S–C) [c]	ν_{sym}(C–S–C)	ν(V ← L) (L = O or N)
$VOBr_2(diox)_2$	994	330s 320w,sh	—	1128, 1104(1125)	876, 859(874)	—	—	
$VOBr_2(thf)_2$	984		—	1012(1069)	857(909)	—	—	
$VOBr_2(hmpa)_2$	989	320s	1189(1218)	—	—	—	—	381m
$VOBr_2(dme)$	890	342s, 326sh	—	1081(1120)	866, 829(858)	—	—	444s
$[VO(Me_2SO)_5]Br_2$	940 [a]	—	940 [a](1040)	—	—	—	—	490vs,br
$VOBr_2(Ph_2SO)_3$	968, 957 [a]	301s, 266m,sh	968, 957 [a] (1042)	—	—	—	—	474s
$VOBr_2(py)_2$	940	334vs	—	—	—	—	—	239w, 233w
$VOBr_2(py)_3$	965, 959	307vs, 257m	—	—	—	—	—	241w, 234w
$VOBr_2(quin)_2$	1012, 993 [b]	342s, 307s	—	—	—	—	—	250w
$VOBr_2(bipy)$	876	355s, 345sh	—	—	—	—	—	258w, 245w
$VOBr_2(tht)_2$	988		—	—	—	665(685)		
$VOBr_2(thiox)_2$	995	347s, 320s	—	1102(1105)	826(826)	684(691)	650(664)	
$VOBr_2(PPh_3)_2$	988	347s, 313m	—	—	—	—	—	

[a] Dual assignment ν(V=O) and ν(S=O). [b] Possibly due to quinoline. [c] Free ligand values in parentheses.

diox = 1,4-Dioxan, hmpa = hexamethylphosphoramide, dme = 1,2-dimethoxyethane, Ph_2SO = diphenyl sulphoxide, py = pyridine, quin = quinoline, bipy = 2,2′-bipyridyl, tht = tetrahydrothiophen, thiox = 1,4-thioxan, Me_2SO = dimethyl sulphoxide.

The products obtained were of one of the following formulations: $VOBr_2L_5$, $VOBr_2L_3$, $VOBr_2L_2$, and $VOBr_2(L-L)$ (where L–L is a bidentate ligand). The i.r. spectra of these complexes are listed in the Table.

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The vanadium–bromine stretching frequencies for the complexes of stoicheiometry $VOBr_2L_3$ are found to be in the region already established for six-co-ordinate complexes.[1] There is no evidence for any of the complexes of stoicheiometry $VOBr_2L_2$ containing either bridging Br or O, and as ν(V–Br) falls in the region previously established for five-co-ordinate complexes [1] it is assumed that all these complexes are monomeric and five-co-ordinate. These complexes have two distinct types of spectrum. One class gives two strong ν(V–Br) stretches, the higher of the two being in the region 360—340 cm^{-1}; the other shows only one ν(V–Br) stretch, in the region 340—320 cm^{-1}. This would be consistent with the latter class having a structure based on the square pyramid, and the former class having a structure based on the trigonal bipyramid. A similar classification was suggested for the $[VOBr_4]^{2-}$ anion, which can exist in C_{2v} and C_{4v} symmetry.[1] It is noteworthy that, for both the six- and five-co-ordinate complexes, the bulkier the ligand, the lower ν(V–Br). The complexes $VOBr_2$(bipy) and $VOBr_2$(dme) have very similar spectra in the ν(V–Br) region (dme = 1,2-dimethoxyethane), which indicates that they also had a five-co-ordinate structure. The complex $[VO(Me_2SO)_5]Br_2$ is ionic, $\nu(V \longleftarrow O)$ being in the expected region.[9,10] No band was observed due to ν(V–Br).

If the oxovanadium(IV) stretching frequencies for the adducts (and anionic complexes [1]) of $VOBr_2$ are examined, the following general trend emerges: $\nu(V{=}O)_{\text{anionic}} > \nu(V{=}O)_{\text{5-co-ord}} > \nu(V{=}O)_{\text{6-co-ord}} > \nu(V{=}O)_{\text{bidentate}}$. The only noticeable exception to this trend is $VOBr_2(py)_2$. Although the bands for $VOBr_2$(bipy) and $VOBr_2$(dme) are of lower frequency than normally found, they are sharp and strong, and not indicative of V=O · · · V interactions.

The i.r. spectra also revealed the mode of bonding of the ligand to the metal. These results are summarised in the Table. The spectra of $VOBr_2(hmpa)_2$, $VOBr_2(Ph_2SO)_3$, and $[VO(Me_2SO)_5]Br_2$ (hmpa = hexamethylphosphoramide) all show a lowering of ν(L=O) (where L = P or S) relative to the free ligand, consistent with co-ordination through the oxygen. For the complexes involving ether ligands, ν(C–O–C) is lowered on co-ordination in every case. The spectrum of $VOBr_2(diox)_2$ is typical of unidentate 1,4-dioxan,[11] and that of $VOBr_2$(dme) is typical of bidentate 1,2-dimethoxyethane.[11,12] No band is observed in the spectrum of $VOBr_2$(dme) at 1338, 936, or 924 cm^{-1}. This shows that the ligand must therefore be bound in its *gauche* conformation,[13] and thus acting as a bidentate chelating ligand. The spectrum of the tetrahydrothiophen complex $VOBr_2(tht)_2$ shows the reported small shift in ν(C–S–C),[14,15] and the spectrum of $VOBr_2(thiox)_2$ is typical of 1,4-thioxan acting as a unidentate ligand co-ordinated through the sulphur.[11]

The electronic spectra of the complexes are listed in the Supplementary Publication. Detailed assignments have not been made, owing to the uncertainty of the ordering of the electronic energy levels in the presence of π-interaction between the vanadium and oxygen. However, the principal *d–d* band in these complexes is apparently influenced by the ligand field. Supplementary Publication No. SUP 20848 (3 pp.) * shows some of the ligand-field correlations. The spectrochemical series for these complexes appears to be O-donors $\sim$ S-donors > P-donors > N-donors. It also appears that the frequency of the band in six-co-ordinate complexes is higher than in the corresponding five-co-ordinate complex. Acetonitrile, as expected, has a large ligand-field effect. Whilst the electronic spectrum of $VOBr_2$(dme) is similar to those of the other complexes, the spectrum of $VOBr_2$(bipy) is very different, and is much more closely similar to the spectra of $VOBr_2$ and of $(pyH)[VOBr_3]$ [1] where much V=O · · · V interaction has been established. Thus, the evidence for the structure of $VOBr_2$(bipy) from i.r. and electronic spectra is conflicting, and no definite conclusion can be reached. The structure of $VOCl_2$(bipy) is likewise unresolved.[16]

On no occasion was a stable adduct of $VOBr_3$ isolated. However, in the reaction between $VOBr_3$ and 2,2′-bipyridyl, a transient dark blue complex was observed; this decomposed during filtration at room temperature to give $VOBr_2$(bipy) and bromine. It was assumed that this dark blue solid was $VOBr_3$(bipy). $VOBr_3$ was also allowed to react with titanium(IV) bromide in n-hexane, and red crystals which melted at temperatures slightly above −20 °C were obtained. These were believed to be a weakly bonded solid phase between $VOBr_3$ and $TiBr_4$, rather than a true complex.

EXPERIMENTAL

Starting Materials.—Vanadium(V) oxide tribromide was prepared by passing bromine over an intimate mixture of vanadium(III) oxide and carbon at 340 °C.[1] All reactions were carried out either under dry nitrogen or *in vacuo.* Titanium(IV) bromide (Alfa) was purified by distillation *in vacuo*. Liquid amines, ether, and sulphur-donor ligands were dried (CaH_2) and purified by distillation. Dimethyl sulphoxide was dried over phosphoric oxide, and the solid ligands (B.D.H. or R. N. Emanuel) were used without further purification. Organic solvents were dried (P_2O_5) and distilled at atmospheric pressure.

Physical Methods and Analyses.—These were as before.[17]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

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Infrared spectra were used to confirm the presence of ligands.

Reactions of $VOBr_3$ *with Tetrahydrofuran.*—(a) *In cyclohexene.* Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of tetrahydrofuran (9·6 cm^3) in cyclohexene (150 cm^3). The resulting emerald green solution was stored at 0 °C for two days. The blue-green *crystals* which formed were filtered off *in vacuo*, washed with cyclohexene (20 cm^3), and dried *in vacuo* (Found: C, 25·6; H, 4·6; Br, 42·6; V, 14·0. Calc. for $C_8H_{16}Br_2O_3V$: C, 25·90; H, 4·35; Br, 43·08; V, 13·73%).

(b) *In neat ligand.* Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to tetrahydrofuran (70 cm^3), giving a dark olive-red solution. Upon storage at 0 °C for several days, the solution slowly became green, and was then reduced in volume to 10 cm^3 *in vacuo*. The mixture was allowed to crystallise slowly at 0 °C for a month, and then the green crystals were filtered off and dried *in vacuo* (Found: C, 25·6; H, 4·35; Br, 42·8%).

Reaction of $VOBr_3$ *with* 1,4-*Dioxan.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of 1,4-dioxan (6·7 cm^3) in cyclohexene (150 cm^3). A yellow-brown solid formed immediately, but upon vigorous shaking the solid slowly became green. The mixture was allowed to stand at 0 °C for eight days, and was then filtered *in vacuo*; the residue was washed with cyclohexene, and dried *in vacuo* to a pale blue *powder* (Found: C, 23·4; H, 4·3; Br, 39·7; V, 13·3. Calc. for $C_8H_{16}Br_2O_5V$: C, 23·84; H, 4·00; Br, 39·66; V, 12·64%); μ_{eff} (20 °C) = 1·90 B.M.

Reaction of $VOBr_3$ *with Hexamethylphosphoramide.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of hexamethylphosphoramide (13·8 cm^3) in cyclohexene (150 cm^3). A green solid formed immediately, and after vigorous shaking it was allowed to stand at 0 °C for three weeks. The blue-green *crystals* were filtered off *in vacuo*, washed with cyclohexene (20 cm^3), and dried *in vacuo* (Found: C, 24·5; H, 6·35; Br, 26·4; N, 14·2; P, 10·4; V, 8·9. Calc. for $C_{12}H_{18}Br_2N_6O_3P_2V$: C, 24·63; H, 6·20; Br, 27·31; N, 14·36; P, 10·59; V, 8·71%); μ_{eff} (20 °C) = 1·68 B.M.

Reaction of $VOBr_3$ *with* 1,2-*Dimethoxyethane.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of 1,2-dimethoxyethane (8·2 cm^3) in cyclohexene (150 cm^3). The mixture was vigorously shaken, and then allowed to stand at 0 °C for five days. The grey-green *powder* was filtered off, washed with cyclohexene (70 cm^3), and dried *in vacuo* (Found: C, 15·4; H, 3·4; Br, 48·9; V, 16·4. Calc. for $C_4H_{10}Br_2O_3V$: C, 15·16; H, 3·18; Br, 50·44; V, 16·08%); μ_{eff} (20 °C) = 1·74 B.M.

Reaction of $VOBr_3$ *with Dimethyl Sulphoxide.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of dimethyl sulphoxide (8·4 cm^3) in cyclohexene (150 cm^3). The mixture was vigorously shaken and allowed to stand at room temperature overnight. The pale green *powder* was filtered off *in vacuo*, washed with cyclohexene (100 cm^3), and dried *in vacuo* (Found: C, 19·6; H, 4·7; Br, 25·4; S, 25·7; V, 8·6. Calc. for $C_{10}H_{30}Br_2O_6S_5V$: C, 19·45; H, 4·90; Br, 25·88; S, 25·96; V, 8·25%); μ_{eff} (20 °C) = 1·74 B.M.

Reaction of $VOBr_3$ *with Diphenyl Sulphoxide.*—Vanadium(v) oxide tribromide (1 cm^3) was added by syringe to a suspension of diphenyl sulphoxide (11·9 g) in cyclohexene (500 cm^3). The heterogeneous mixture was allowed to stand at 0 °C for a month, with occasional vigorous shaking, during which a homogeneous blue *powder* formed. This was filtered off *in vacuo*, washed with cyclohexene (50 cm^3), and dried *in vacuo* (Found: C, 52·1; H, 3·8; S, 11·5; V, 6·2. Calc. for $C_{36}H_{30}Br_2O_4S_3V$: C, 51·87; H, 3·63; S, 11·54; V, 6·11%).

Reaction of $VOBr_3$ *with Pyridine.*—(a) 1 : 4 *Mole ratio.* Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of pyridine (6·3 cm^3) in cyclohexene (150 cm^3). After vigorous shaking, the mixture was allowed to stand at 0 °C for one week. The slate-blue *powder* was filtered off and dried *in vacuo* (Found: Br, 35·1; V, 10·9. Calc. for $C_{15}H_{15}Br_2N_3OV$: Br, 34·44; V, 10·98%); μ_{eff} (20 °C) = 1·69 B.M.

(b) 1 : 2 *Mole ratio.* The above reaction was carried out with 3·15 cm^3 of pyridine. The product was a pale green-blue *powder* (Found: Br, 40·6; V, 12·8. Calc. for $C_{10}H_{10}Br_2N_2OV$: Br, 41·52; V, 13·23%); μ_{eff} (20 °C) = 1·61 B.M.

Reaction of $VOBr_3$ *with Quinoline.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of quinoline (6·95 cm^3) in cyclohexene (150 cm^3). A dark green precipitate formed immediately, and was allowed to stand at 0 °C for a week. The powder was filtered off *in vacuo*, washed with cyclohexene (100 cm^3), and dried *in vacuo* (Found: C, 44·3; H, 3·1; Br, 33·5; N, 5·64; V, 10·2. Calc. for $C_{18}H_{14}Br_2N_2OV$: C, 44·57; H, 2·91; Br, 32·95; N, 5·77; V, 10·50%); μ_{eff} (20 °C) = 1·63 B.M.

Reaction of $VOBr_3$ *with* 2,2′-*Bipyridyl.*—Vanadium(v) oxide tribromide (1 cm^3) was added by syringe to a solution of 2,2′-bipyridyl (9·2 g) in cyclohexene (150 cm^3). A dark blue precipitate formed instantly, and was immediately filtered off *in vacuo*. The solid was washed with cyclohexene (200 cm^3), and decomposed on the sinter to give a green solid and a red filtrate. Washing was continued until the filtrate was colourless, and the *solid* was dried *in vacuo* (Found: C, 31·0; H, 2·1; Br, 42·7; N, 7·1; V, 13·3. Calc. for $C_{10}H_8Br_2N_2OV$: C, 31·36; H, 2·11; Br, 41·73; N, 7·31; V, 13·30%); μ_{eff} (20 °C) = 1·68 B.M.

If the mixture was allowed to stand for more than a few minutes before filtration, the decomposition to the green product occurred in the reaction mixture. Under those conditions, products were isolated of composition $VOBr_2(bipy)_x$, where x = 1·3—1·7. However, even after several weeks' reaction, $VOBr_2(bipy)_2$ was not isolated.

Reaction of $VOBr_3$ *with Tetrahydrothiophen.*—Vanadium(v) oxide tribromide (2 cm^3) was added by syringe to a solution of tetrahydrothiophen (10·8 g) in cyclohexene (150 cm^3). The resulting emerald green solution was stored at 0 °C overnight. The blue-green *crystals* were filtered off *in vacuo*, washed with cyclohexene (30 cm^3), and dried *in vacuo* for many hours (Found: C, 23·7; H, 3·9; Br, 39·6; S, 15·7; V, 13·1. Calc. for $C_8H_{16}Br_2OS_2V$: C, 23·84; H, 4·00; Br, 39·65; S, 15·91; V, 12·63%).

Reaction of $VOBr_3$ *with* 1,4-*Thioxan.*—Vanadium(v) oxide tribromide (2·7 cm^3) was added by syringe to a solution of 1,4-thioxan (16·6 g) in cyclohexene (150 cm^3). The mixture was vigorously shaken and then stored at 0 °C for two days. The green *powder* was filtered off *in vacuo*, washed with cyclohexene (30 cm^3), and dried *in vacuo* for many hours (Found: C, 22·0; H, 3·6; Br, 37·0; S, 14·6; V, 11·5. Calc. for $C_8H_{16}Br_2O_3S_2V$: C, 22·08; H, 3·71; Br, 36·73; S, 14·74; V, 11·71%).

Reaction of $VOBr_2(MeCN)_3$ *with Triphenylphosphine.*—A solution of triphenylphosphine (18 g) in tetrahydrofuran (75 cm^3) was added to a solution of oxodibromotris(acetonitrile)vanadium(IV)[1] (4 g) in tetrahydrofuran (50 cm^3).

The solution was stored at 0 °C for three days, concentrated to 20 cm^3 *in vacuo*, and then stored at 0 °C for a further two days. The green *solid* formed was filtered off *in vacuo*. washed with cyclohexene (250 cm^3), and dried *in vacuo* (Found: C, 57·3; H, 4·1; Br, 20·8; P, 8·0; V, 7·0. Calc, for $C_{36}H_{30}Br_2OP_2V$: C, 57·55; H, 4·02; Br, 21·27; P, 8·24; V, 6·78%); μ_{eff} (20 °C) = 1·81 B.M.

Reaction of $VOBr_3$ *with Titanium*(IV) *Bromide*.—Vanadium(V) oxide tribromide (0·76 cm^3) was condensed into a solution of titanium(IV) bromide (2·75 g) in n-hexane (40 cm^3). The mixture was allowed to warm to room temperature, and the red solution was concentrated to about 3 cm^3 *in vacuo*. The resulting solution was stored at −20 °C, whence red crystals formed. These melted when allowed to warm slightly.

We thank the Physico-Chemical Measurements Unit at Harwell for measuring the far-i.r. spectra and the S.R.C. for a maintenance grant (to K. R. S.).

[3/1361 *Received*, 28*th June*, 1973]