Reactions of Vanadium(V) Oxide Tribromide: Preparation and Properties of Complex Oxobromovanadates(IV)

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The reactions of $VOBr_3$ with various ionic bromides, acetonitrile, nitromethane, and ferrocene are reported. The following new complexes were prepared and their structure investigated: $(Et_4N)_2[VOBr_4]$, $(pyH)[VOBr_3]$, $(pyH)[VOBr_3(CH_3CN)_2]$, $(pyH)_2[VOBr_4]$, $(quinH)_3[VOBr_5]$, $[Fe(cp)_2][VOBr_3]$, and $VOBr_2(CH_3CN)_3$ (py = pyridine, quin = quinoline, and cp = π-cyclopentadienyl). The first detailed study of the far-i.r. spectra of vanadium(IV) oxide dibromide complexes is reported, and evidence for a novel reversible transformation between C_{2v} and C_{4v} symmetry for the $[VOBr_4]^{2-}$ anion is presented.

SINCE its discovery in 1870[1,2] vanadium(V) oxide tribromide has remained virtually unstudied. The principal reason for this is that the literature preparations[1–5] have either proved unrepeatable or give only very small yields. Apart from hydrolysis and thermal decomposition, the only reactions of $VOBr_3$ which have been studied are with ozone (to give $V_4O_9Br_2$)[6] and with PBr_5 (to give $VBr_3,POBr_3$).[7] The physical properties of $VOBr_3$ have been reviewed,[8] and its Raman spectrum has been published.[9] We have developed a method of preparation, based on that of Loomis and Schlundt,[3] which gives a 30—40 g yield of $VOBr_3$ (*ca.* 30% based upon V_2O_5), and report its reactions with various ionic bromides, ferrocene, acetonitrile, and nitromethane. In every case, reduction to vanadium(IV) occurred. The first reported anionic complex oxobromovanadates(IV) have been isolated from these systems.

RESULTS AND DISCUSSION

Whereas oxochlorovanadates(IV), *e.g.*, containing the ions $VOCl_3^-$ or $VOCl_4^{2-}$ are well characterised,[10,11] no oxobromovanadate(IV) has been isolated. Attempts to prepare such complexes by reduction of vanadium(V) species in aqueous hydrogen bromide have led to the isolation of bromoaquovanadates(III).[12] Gutmann and Laussegger[13] have presented spectrophotometric, potentiometric, and conductimetric evidence for the formation of oxobromovanadium(IV) ions when $VOBr_2$ dissolves in co-ordinating solvents.

When $VOBr_3$ reacted with various ionic bromides in acetonitrile and/or nitromethane, and with ferrocene in n-hexane, the complexes listed in the Table were obtained; their molar conductivities were recorded in acetonitrile at 25 °C. Their i.r. spectra are listed in the Table and electronic spectra in Supplementary Publication No. SUP 20847 (2 pp.).† When V^V is reduced to V^{IV} by bromide ions, free bromine is liberated. It is this bromine liberated during the reduction which is responsible for the preparative difficulties in the synthesis of the oxobromovanadium(IV) complexes. Unless the conditions of reaction (*e.g.*, temperature and relative

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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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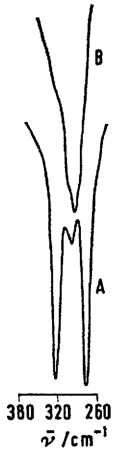
concentrations) were very carefully regulated, perbromides were formed. With many counterions (such as tetrabutylammonium and ethyltriphenylphosphonium), organic perbromides were the only products isolated from the reaction mixtures. The reaction between $VOBr_3$ and pure acetonitrile (the solvent most commonly used in the reactions studied) gave impure products (typically V : Br *ca.* 1 : 2·3). However, when the reaction was carried out in cyclohexene, a product corresponding to $VOBr_2(MeCN)_3$ was isolated. The reaction between $VOBr_3$ and nitromethane yielded impure $VOBr_2$.

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

	ν(V–Br)	ν(V–Br)$_{bridg.}$	ν(V=O)	ν(C≡N)	Ligand or cation bands (400—200 cm^{-1})	Unassigned	Other bands	$(\Lambda_M)_0$/ Ω^{-1} cm^2	No. of ions [e]
$(Et_4N)_2[VOBr_4]$	{325s,[a] 300w,[a] 274s[a], 296[b]}	—	{991[a] 998[b]}	—	202m	—	—	365	3
$(pyH)[VOBr_3(MeCN)_2]$	320vs, 298vs	—	984	2325,[d] 2320,[d] 2300, 2280	384m	201m	223w ν(V–N)	167	2
$(pyH)[VOBr_3]$	319s	248m, 228m	998	—	387s	—	862 ν(V=O · · · V)		
$(quinH)_3[VOBr_5]$	228m, 268/260s	—	1007, 998, 990[c]	—	387m, 370sh, 203w	338s	—	433	4
$[Fe(cp)_2][VOBr_3]$	388s, 330m	—	1000	—	—	544w	295s δ(O–V–Br)	122	2
$VOBr_2(MeCN)_3$	316s, 263m	—	978	2320,[d] 2295	—	201w	232w ν(V–N)	46	0
$(pyH)_2[VOBr_4]$			999	—				313	3
$VOBr_2$								182[f]	2

[a] At − 30 °C. [b] At + 35 °C. [c] Possibly due to quinolinium ion. [d] Combination (CH_3 bend and C–C stretch) modes. [e] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81. [f] Based on $[VOBr(MeCN)_2][VOBr_3(MeCN)_2]$.

With the exception of $VOBr_2(qn)_2$ (where qn = quinuclidine),[14] whose structure is uncertain, there is no far-i.r. datum in the literature on vanadium(IV) oxide dibromide complexes. Thus, it was necessary to establish the i.r. spectral region in which ν(V–Br) would be expected for four-, five-, and six-co-ordinate structures [it is well established that ν(M–X) decreases as co-ordination number about the metal increases[15,16]]. Examination of the Table, with an elementary consideration of stoicheiometry (*N.B.* in no case was there any evidence for lattice-held acetonitrile), indicates that the complexes $VOBr_2(MeCN)_3$, $(pyH)[VOBr_3(MeCN)_2]$, $(quinH)_3[VOBr_5]$, and $(pyH)[VOBr_3]$ contain vanadium in a pseudo-octahedral environment, the highest ν(V–Br) usually being between 320 and 300 cm^{-1} but becoming much lower for the triply negatively charged ion $[VOBr_5]^{3-}$. The far-i.r. spectrum of $(Et_4N)_2[VOBr_4]$ shows a complete and reversible transformation within the temperature range 20—35 °C. The Figure illustrates the spectrum in the region between 380 and 260 cm^{-1} at 20 and 35 °C. The change was shown to be completely reversible by recording the spectrum (of the same sample) at −30, +35, and then finally at −30 °C. There was no significant difference between the two −30 °C spectra and the spectrum recorded at 20 °C. The reason for this transformation will now be considered. The vacuum thermogram of the complex showed it to be thermally stable up to 300 °C, so that decomposition of the complex can be discounted. This means that the change must involve a structural transformation. As the region for ν(V–Br) is that which would be expected for a five-co-ordinate vanadium(IV) ion with a double negative charge (by comparison with the region established above for six-co-ordinate complexes), the most likely interpretation is that a change in symmetry of the ion has occurred. The possibility of dimerisation to give a six-co-ordinate species can be eliminated since the i.r. spectrum at the higher temperature shows no band attributable to either V=O · · · V or V–Br–V interactions. The coalescence of the two peaks to one peak would be consistent with equilibrium (1). A small percentage of the C_{4v} species at −30 °C would account for the weak peak at 300 cm^{-1}. It is well established that C_{4v} species of this type (*e.g.*, $[TiCl_4]^{2-}$[17] and $[InCl_5]^{2-}$[18]) show only one strong band, while C_{2v} species [*e.g.*, $VOCl_2$-



I.r. spectrum of $(Et_4N)_2[VOBr_4]$ at A, 20 °C and B, 35 °C

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[14] R. J. H. Clark and G. Natile, *Inorg. Chim. Acta*, 1970, **4**, 533.

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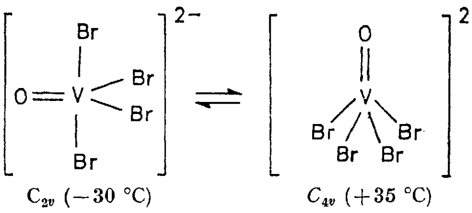
$(NMe_3)_2$[17]] show two strong ν(M–X) bands. A similar transformation between C_{2v} and C_{4v} symmetry has recently been suggested for $[VOF_4]^-$.[19]



(1)

The i.r. spectrum of $[Fe(cp)_2][VOBr_3]$ is also very interesting. Like that of its chloro-analogue,[20] the i.r. spectrum of the complex is characteristic of ferricenium rather than ferrocene.[21] The position of ν(V–Br) at 388 cm^{-1} [*cf.* ν(V–Br) at 400 cm^{-1} for $VOBr_3$ [5]] and the absence of a ν(V=O · · · V) band strongly indicates that the anion has a pseudo-tetrahedral structure. This is in contrast with the spectrum of $(pyH)[VOBr_3]$, which apparently contains a six-co-ordinate polymeric anion (the i.r. spectrum indicating both bridging Br and O).

The electronic spectra (both diffuse reflectance and solution) of the complexes are listed in Supplementary Publication No. SUP 20847 (2 pp.). Because these spectra are dominated by transitions involving the energy level derived from the π-interaction between V and O, very little information of structural significance can be obtained. No detailed assignment of the spectra has been made owing to the uncertainty of the ordering of the electronic energy levels, although simple assignments on Drake, Vekris, and Wood's scheme [22] for $[VOCl_4]^{2-}$ could be made. However, there are several interesting features deserving of comment. In general, the spectra of $[VOBr_3(MeCN)_2]^-$ and $[VOBr_4]^{2-}$ are analogous to those of their chloro-counterparts.[11,22,23] The electronic spectrum of $[Fe(cp)_2][VOBr_3]$ shows the characteristic bands of the ferricenium ion,[24] and also a band at 11·2 kK ($\varepsilon_{max.} = 234$) consistent with $[VOBr_3]^-$ having a pseudo-tetrahedral structure (even in solution in acetonitrile). The behaviour of $(quinH)_3VOBr_5$ was unique amongst these complexes in that the spectrum completely changed on dissolution in acetonitrile. The reflectance spectrum is totally different from that reported for $[VOCl_5]^{3-}$, which showed a principal $d \leftrightarrow d$ band at 15·5 kK,[25] but was similar in band shape to the principal $d \leftrightarrow d$ band of $[VO(Me_2SO)_5]Br_2$.[26] Since $[VO(Me_2SO)_5]Br_2$ has absorption bands at 15·0sh, 11·9, and 9·0sh kK, it seems unlikely that the spectrum reported for $VOCl_5^{3-}$ is in fact due to the $VOCl_5^{3-}$ ion; no solid containing this ion has been isolated. A final point of interest is that the solution spectra and conductivity of $VOBr_2$ and $VOBr_2(MeCN)_3$ in acetonitrile are very different. The low conductivity, and similarity in the reflectance and solution spectra of $VOBr_2(MeCN)_3$, suggests that this exists as $VOBr_2(MeCN)_3$ in solution. However, the conductivity of $VOBr_2$ in acetonitrile and the band at 12·9 kK ($\varepsilon_{max.} = 166$) would indicate it had dissolved as $[VOBr(MeCN)_2]^+[VOBr_3(MeCN)_2]^-$. Similar ionisations have also been reported for other halides of Groups III and V.[27]

In conclusion, we summarise many of the attempted preparations of oxo-bromo vanadium(IV) complexes that were unsuccessful. Attempts to prepare $(Et_4N)[VOBr_3(MeCN)_2]$, $(quinH)_2[VOBr_4]$, and $(pyH)_2[VOBr_4]$ in acetonitrile by varying the mole ratios of the reactants failed. However, there are similar anomalies in the chloro-system which remain unexplained. Reaction of pyridine and quinoline with $VOBr_3$ in ethanolic HBr led only to the formation of organic perbromides. The reaction of $VOBr_3$ with neat NOBr yielded only $VOBr_2$, and a similar reaction carried out in 1,2-dibromoethane yielded unrepeatable non-stoicheiometric nitrogen monoxide adducts of $VOBr_2$.

EXPERIMENTAL

Starting Materials.—Nitrosyl bromide was prepared by the method described in Brauer [28] and purified by the method of Burns and Bernstein.[29] The alkylammonium bromides and hydrobromides of organic bases were thoroughly dried *in vacuo* before use. Organic solvents were fractionally distilled from phosphoric oxide. Ferrocene (B.D.H.) was used without further purification.

Physical Methods and Analyses.—These were performed as described previously.[7] I.r. spectra were used to confirm the presence of the cations and ligands.

Preparation of Vanadium(V) *Oxide Tribromide.*—An intimate mixture of vanadium(V) oxide and carbon was prepared by gently heating a mixture of vanadium(V) oxide (30·3 g) and sucrose (9·5 g) in a loosely covered vessel until carbonisation was complete. This mixture was packed into a combustion tube and heated in a stream of hydrogen for 2 h at 500 °C. The mixture was then allowed to cool in hydrogen to 330 °C. Bromine (carried in a stream of nitrogen) was passed over the vanadium(III) oxide–carbon mixture at 340 ± 5 °C for 8 h. Temperature control was important at this stage; at slightly higher temperatures the principal product was vanadium(III) bromide, at lower temperatures the yield of vanadium(V) oxide tribromide was greatly reduced. The $VOBr_3$ was collected in a U-tube cooled in ice. It was separated from excess of bromine and solid reaction products by fractionation *in vacuo* (yield 30—40 g). Because of the rapid hydrolysis in moist air, all reactions of $VOBr_3$ were carried out either in dry nitrogen or *in vacuo*.

Reaction of $VOBr_3$ *with Tetraethylammonium Bromide.*—Vanadium(V) oxide tribromide (3·4 cm^3) was added by

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syringe to a solution of tetraethylammonium bromide (14 g) in acetonitrile (300 cm^3). The resulting emerald green solution was concentrated to 125 cm^3 *in vacuo* and kept at 0 °C for two weeks. The emerald green crystals which formed were filtered off *in vacuo*, washed twice with acetonitrile (10 cm^3), and dried *in vacuo* (Found: Br, 49·5; V, 8·2. Calc. for $C_{16}H_{40}Br_4N_2OV$: Br, 49·40; V, 7·87%); μ_{eff} (20 °C) = 1·79 B.M.

In a similar preparation, nitromethane (200 cm^3) was used as solvent for tetraethylammonium bromide (10 g) and vanadium(V) oxide tribromide (2 cm^3). Concentration *in vacuo* and cooling of the solution to 0 °C again gave emerald green *crystals* (Found: Br, 48·7; V, 8·15%).

Reaction of $VOBr_3$ *with Pyridinium Bromide*.—(a) *In acetonitrile*. Vanadium(V) oxide tribromide (3·4 cm^3) was added by syringe to a solution of pyridinium bromide (10·7 g) in acetonitrile (250 cm^3). The resulting green solution was kept at 0 °C for two weeks. The blue *crystals* which formed were filtered off *in vacuo*, washed with acetonitrile (10 cm^3), and dried *in vacuo* (Found: Br, 51·2; V, 11·1. Calc. for $C_9H_{12}Br_3N_3OV$ requires Br, 51·13; V, 10·86%); μ_{eff} (20 °C) = 1·76 B.M.

(b) *In nitromethane*. Vanadium(V) oxide tribromide (1·7 cm^3) was added by syringe to a solution of pyridinium bromide (5·3 g) in nitromethane (150 cm^3). After vigorous shaking, the blue-green solution was kept at 0 °C for several weeks. The green *crystals* which formed were separated from the fine powder (which was the major reaction product) with fine tweezers, rinsed with nitromethane, and dried *in vacuo* (Found: Br, 52·9; V, 8·80. Calc. for $C_{10}H_{12}Br_4N_2OV$: Br, 58·46; V, 9·32%).

Reaction of $VOBr_3$ *with Quinolinium Bromide*.—Vanadium(V) oxide tribromide (3·4 cm^3) was added by syringe to a solution of quinolinium bromide (14 g) in acetonitrile (500 cm^3). The resulting green solution was kept at 0 °C for a month. The dark green *crystals* which formed were filtered off *in vacuo*, washed with acetonitrile (20 cm^3), and dried *in vacuo* (Found: C, 38·1; H, 3·05; Br, 42·5; N, 4·8; V, 6·0. Calc. for $C_{27}H_{24}Br_5N_3OV$: C, 37·84; H, 2·82; Br, 46·62; N, 4·90; V, 5·94%); μ_{eff} (20 °C) = 1·59 B.M.

Reaction of $VOBr_3$ *with Ferrocene*.—Vanadium(V) oxide tribromide (1·7 cm^3) was added by syringe to a solution of ferrocene (3·1 g) in n-hexane (300 cm^3). A dark green heterogeneous solid was immediately formed, and was allowed to stand at 0 °C for two weeks. The now homogeneous green *powder* was filtered off *in vacuo*, washed several times with n-hexane and dried *in vacuo* (Found: C, 24·1; H, 2·3; Br, 48·4. Calc. for $C_{10}H_{10}Br_3FeOV$: C, 24·38; H, 2·05; Br, 48·66%); μ_{eff} (20 °C) = 3·48 B.M.

Reaction of Nitrosyl Bromide with $VOBr_3$.—Vanadium(V) oxide tribromide (9 cm^3) was added by syringe to liquid nitrosyl bromide (89 g) at −35 °C. A dark precipitate formed immediately, with no effervescence, and was filtered off at −30 °C *in vacuo*. The olive-brown *powder* was then dried *in vacuo* at room temperature (Found: Br, 69·3; V, 21·7. Calc. for Br_2OV: Br, 70·48; V, 22·46%); μ_{eff} (20 °C) = 1·38 B.M.

Preparation of Pyridinium Oxotribromovanadate(IV).—Pyridinium oxotribromobis(acetonitrile)vanadate(IV) (2·5 g) was heated *in vacuo* at 80—85 °C for 14 h. The vapour evolved during the thermal decomposition was identified as acetonitrile; the residue was a slate-blue *powder* (Found: Br, 59·4; V, 13·4; weight loss, 17·2. Calc. for $C_5H_6Br_3NOV$: Br, 61·98; V, 13·17%; its formation from the previous complex corresponds to a weight loss of 17·5%); μ_{eff} (20 °C) = 1·76 B.M.

Reaction of $VOBr_3$ *with Acetonitrile*.—Vanadium(V) oxide tribromide (4 cm^3) was added by syringe to a solution of acetonitrile (8·2 cm^3) in cyclohexene (150 cm^3). A dark oil formed, which slowly solidified on standing for several days at 0 °C. The solid was broken up and well shaken with the solvent, and then kept at 0 °C for a further two days. The dark blue-green *solid* was filtered off *in vacuo*, washed with cyclohexene (100 cm^3), and dried *in vacuo* for 48 h (Found: Br, 45·3; V, 14·9. Calc. for $C_6H_9Br_2N_3OV$: Br, 45·67; V, 14·56%); μ_{eff} (20 °C) = 1·77 B.M. In a similar preparation, the product was evacuated for only 6 h (Found: Br, 44·5; V, 14·4%). This behaviour has been reported for other acetonitrile complexes.[7]

Reaction of $VOBr_3$ *with Nitromethane*.—Vanadium(V) oxide tribromide (2 cm^3) was added by syringe to nitromethane (70 cm^3), and the mixture was vigorously shaken. The dark green solution was allowed to stand at 0 °C for three days, and the olive solid which was formed was filtered off *in vacuo*, washed with nitromethane (20 cm^3), and dried *in vacuo* (Found: Br, 64·9; V, 21·6. Calc. for Br_2OV: Br, 70·48; V, 22·46%); i.r. spectrum indicated lattice-held nitromethane, which could not be removed by prolonged evacuation.

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