

## Vanadium(II) Complex Bromides

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**Summary:** The bromide complexes  $M_2 [VBr_4]$ , where  $M = NPhH_3, NEt_3, NMe_2H_2, n-C_8H_{17}, C(NH_2)_3, M_2 [VBr_6]$  where  $M = H_2 pipz$  and  $CsVBr_3$  have been prepared and investigated by magnetic and electronic spectral measurements down to liquid nitrogen temperatures, and by i.r. spectra. The compounds have octahedral polymeric structures, containing sheets of planar  $[VBr_4]^{2-}$  units. The compounds are antiferromagnetic. Their reflectance spectra contain more bands than expected from  $O_h$  symmetry, but this is probably due to the presence of anomalously-intense, spin-forbidden bands rather than to deviations from  $O_h$  symmetry.

### Introduction

The halide complexes of vanadium(II) have received scant attention, presumably because of the difficulty of handling them and of obtaining the parent hydrated halide. The double chlorides have been previously reported and characterised [1]. We present magnetic, i.r., electronic spectral and structural results on a series of vanadium(II) bromide complexes.

### Results and Discussion

The compounds were obtained from aqueous solutions [2] of vanadium(II) bromide, prepared electrolytically, and the appropriate bivalent bromide. All operations were carried out under nitrogen.

**Magnetic measurement:** The variation with temperature, in the range 90-300K, of the atomic susceptibilities,  $\chi_A$ , and the effective magnetic moments,  $\mu_{eff}$ , of the complexes are shown in Tables 1-2 and Figures 1-2.  $[NPhH_3]_2 [VBr_4]$ ,  $[NEtH_3]_2 [VBr_4]$  and  $[n-C_8H_{17}NH_3]_2 [VBr_4]$  have effective magnetic moments somewhat slightly below the spin-only value of 3.87 B.M. at room temperature. All other tetrabromovanadates(II), including caesium tribromovanadate(II) have effective magnetic moments,  $\mu_{eff}$ , considerably lower than the spin-only value which decreases markedly with decrease in temperature. This is ascribed to antiferromagnetic interactions within bromide-bridged structures.

**Electronic spectra:** The diffuse reflectance spectra of the bromovanadates(II) are shown in

Figures 3-4. The energies of the bands, their assignments and electron repulsion parameters are listed in Table 3. The Racah parameter  $B'$  was deduced

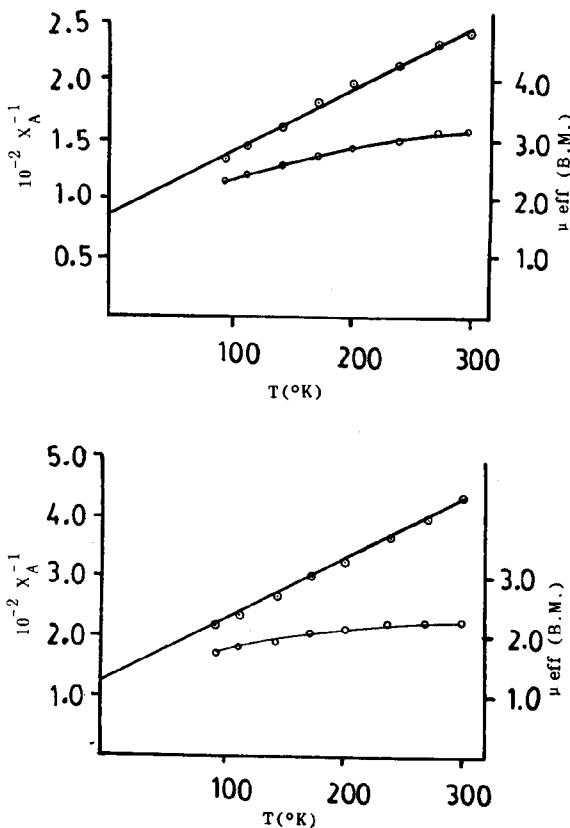


Fig. 1-2: Variation with temperature of experimental reciprocal molar susceptibilities of  $[NMe_2H_2]_2 [VBr_4]$  and  $[n-C_8H_{17}NH_3]_2 [VBr_4]$ .

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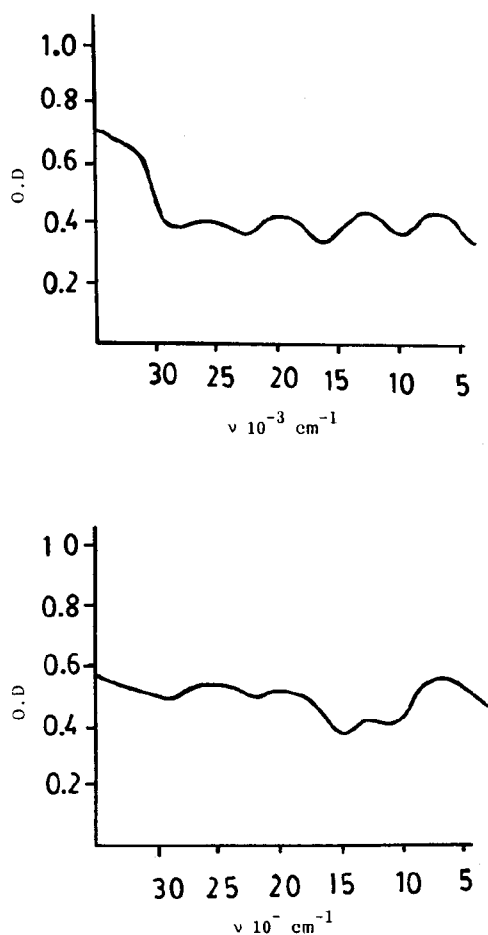


Fig. 3-4: Reflectance Spectra of  $[\text{NPhH}_3]_2 [\text{VBr}_4]$  and  $[\text{NEtH}_3]_2 [\text{VBr}_4]$  at room temperature.

from the relationships  $15B' = \nu_2 + \nu_3 - 3\nu_1$  (the diagonal sum rule) and then positions of  $\nu_2$  and  $\nu_3$  were calculated from the secular determinant [4]. The  $B'$  values are comparable with the free ion values of  $755 \text{ cm}^{-1}$  except ethylammonium-, anilinium-, octylammonium-, and guanidinium tetrabromovanadates(II), the values of which are smaller which may be due to the increase of metal-ligand covalency. The calculated and experimental values of  $\nu_2$  and  $\nu_3$  agree in all cases. The spectra suggest approximately octahedral symmetry presumably achieved via bridging bromide, although the bands in some spectra were weak and broad and it was difficult to assign values to  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ .

For  $d^3$  or  $d^8$  complexes with  $O_h$  symmetry, as  $10Dq$  increases, configuration interaction between the high spin  $T_{1g}(\text{P})$  and  $T_{1g}(\text{F})$  excited states gradually lowers the ratio  $\nu_2/\nu_1$  from the theoretical value of 1.80 to ca. 1.5-1.7. The values of  $\nu_2/\nu_1$  in the bromovanadates(II) are in the range of 1.54-1.82, typical of octahedral vanadium(II) [1]. The reflectance spectra of all the compounds show three spin allowed bands which are very broad (half-width  $\approx 2000 \text{ cm}^{-1}$ ). The strong and broad bands in the range of  $7000 \text{ cm}^{-1}$  in the spectra of the tetrabromovanadates(II) and caesium tribromovanadate(II) and at  $8200 \text{ cm}^{-1}$  in caesium tribromovanadate(II) correspond to the transition to  ${}^4T(\nu_1)$ , medium bands in the range  $12300-12800 \text{ cm}^{-1}$  for the tetrabromovanadates(II), and at  $13000 \text{ cm}^{-1}$ , for the caesium tribromovanadate(II) correspond to the transition to  ${}^4T(\text{F})$ , and shoulders in the range  $19800-20500 \text{ cm}^{-1}$  in the tetrabromovanadates(II) and caesium tribromovanadate(II), to  ${}^4T(\text{P})$  transition. The  $\nu_1$  band of the dimethylammonium tetrabromovanadate(II) appears to be split into two components  $9600$  and  $7200 \text{ cm}^{-1}$ . These may be assigned to the transition  ${}^4B_{1g} \rightarrow {}^4B_{2g}$  and  ${}^4B_{1g} \rightarrow {}^4E_g$  respectively.

*Far-i.r. Spectra:* The far infra-red bands are given in Table 4. The spectra in the region  $4000-600 \text{ cm}^{-1}$  have not been reported because they show bands due to organic cations only. The strong bands observed in the region  $210-225 \text{ cm}^{-1}$  in the spectra of the tetrabromovanadates(II), and at  $240 \text{ cm}^{-1}$  in  $\text{C}_3\text{VBr}_3$  can be assigned to  $\nu(\text{V-Br})$  stretching vibrations since these bands are somewhat lower than the range assigned to the chlorovanadates(II) [1]. The stretching frequencies of the tetrabromovanadates(II) are somewhat lower than those of the tetrabromochromates(II) which have these bands in the range of  $230-260 \text{ cm}^{-1}$  [5]. This may be due to different metal halide bond lengths. It is likely that the V-Br bond lengths are equal while the tetrabromochromates(II) have four short and two long Cr-Br bonds.

*Structures:* Although, little detailed structural information has been reported, the bromovanadates(II) are known to have octahedral polymeric structures, containing sheets of bromide bridged square planar  $[\text{VBr}_4]^{2-}$  units in which the V-Br distances are equal, with amine cations lying

Table 1: Analytical and Magnetic Data

Compound and Colour	Analysis % <sup>a</sup>					Magnetic properties		
	V	Br	C	H	N	T/K	$\mu_{\text{eff}}^b$ B.M.	Diamagnetic <sup>c</sup> corrections/c.g.s. Units x 10 <sup>6</sup>
[NC <sub>6</sub> H <sub>8</sub> ] <sub>2</sub> [VBr <sub>4</sub> ] Greyish orange	8.81 (9.12)	57.69 (57.22)	26.2 (26.6)	3.26 (2.89)	3.69 (5.06)	295 90	3.24 2.25	-269
[NC <sub>2</sub> H <sub>6</sub> ] <sub>2</sub> [VBr <sub>4</sub> ] Grey	10.38 (11.01)	69.33 (69.09)	10.01 (10.37)	3.45 (3.80)	4.76 (6.05)	295 90	3.12 2.37	-220
[NC <sub>2</sub> H <sub>8</sub> ] <sub>2</sub> [VBr <sub>4</sub> ] Khaki	11.24 (11.01)	69.40 (69.09)	10.34 (10.37)	3.86 (3.45)	5.70 (6.05)	295 90	2.34 1.80	-220
[NCaH <sub>20</sub> ] <sub>2</sub> [VBr <sub>4</sub> ] Pale grey	7.78 (8.07)	50.31 (50.68)	29.09 (30.45)	6.61 (6.34)	4.44 (3.92)	295 90	3.13 2.29	-362
[N <sub>2</sub> C <sub>4</sub> H <sub>14</sub> ] <sub>2</sub> [VBr <sub>6</sub> ] Light yellow	6.49 (7.71)	66.96 (67.48)	15.14 (15.72)	3.81 (4.58)	8.53 (9.17)	295 90	2.35 2.13	-288
[N <sub>3</sub> CH <sub>6</sub> ] <sub>2</sub> [VBr <sub>4</sub> ] Grey	10.62 (10.38)	65.49 (65.15)	5.36 (4.89)	3.40 (2.44)	16.78 (17.12)	295 90	2.41 1.75	-210

<sup>a</sup>Calculated values in parentheses. <sup>b</sup>Calculated from  $\mu_{\text{eff}} = 2.828 (\chi_{\text{AT}})^{1/2}$ . <sup>c</sup>Susceptibility also corrected for temperature-independent paramagnetism by subtraction of  $100 \times 10^{-6}$  c.g.s. units.

between the sheets as shown in Fig. 5. Comparisons of the powder photographs of ethylammonium tetrabromovanadate(II) and ethylammonium tetrabromochromate(II) show that the two compounds are not isomorphous as might be expected because the tetrabromochromates(II) probably contain four short and two long Cr-Br bonds. The structure of compound CsVBr<sub>3</sub> consists of linear chains of regular VBr<sub>6</sub> octahedra linked at their faces, as shown in Fig. 6.

**Other Investigations:** The complexes [NMe<sub>2</sub>H<sub>2</sub>]<sub>2</sub> [VBr<sub>4</sub>] and [n-C<sub>8</sub>H<sub>17</sub>NH<sub>3</sub>]<sub>2</sub> [VBr<sub>4</sub>] have molar conductances in 0.001 mol dm<sup>-3</sup> ethanolic solutions of 124 and 81 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively. The value for the former compound indicates partial dissociation of bromide ions in solutions.

### Experimental

All preparations and measurements were carried out under nitrogen. The compounds were dried under continuous pumping.

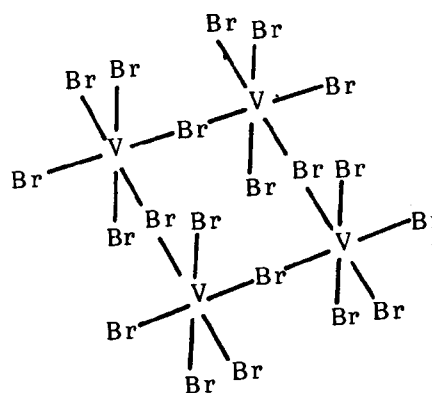


Fig. 5: Structure showing sheets of bromide bridged square planar [VBr<sub>4</sub>]<sup>2-</sup> units.

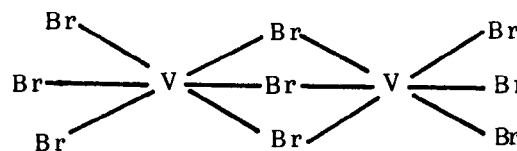


Fig. 6: Structure of CsVBr<sub>3</sub> showing linear chains of regular VBr<sub>6</sub> octahedra.

**Table 2: Variation of corrected molar susceptibilities of tetrabromovanadates(II) with absolute temperature**

Compound	T(°K)	10 <sup>6</sup> χ <sub>A</sub>
[NPhH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	295.5	4,451
	265.3	4,685
	229.5	5,018
	197.3	5,312
	166.5	5,755
	135.3	6,308
	104.0	6,825
	89.5	7,132
	[NEtH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	295.5
265.5		4,475
229.5		4,828
197.4		5,195
166.5		5,706
135.3		6,441
104.0		7,312
89.5		7,888
[NMe <sub>2</sub> H <sub>2</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]		295.3
	265.5	2,508
	229.5	2,727
	197.4	2,991
	166.5	3,279
	135.3	3,693
	104.0	4,233
	89.5	4,544
	[n-C <sub>8</sub> H <sub>17</sub> NH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	295.5
265.5		4,384
229.5		4,720
197.4		5,119
166.5		5,570
135.3		6,395
104.0		6,998
89.5		7,366
(H <sub>2</sub> pipz) <sub>2</sub> [VBr <sub>6</sub> ]	295.5	2,348
	265.5	2,593
	229.5	2,979
	197.4	3,248
	166.5	3,775
	135.3	4,606
	104.0	5,682
	89.5	6,349
[C(NH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	295.5	2,458
	265.4	2,596
	229.5	2,834
	197.4	3,002
	166.5	3,230
	135.3	3,656
	104.0	4,111
	89.5	4,319

**Continued Table II:**

Compound	T(°K)	10 <sup>6</sup> χ <sub>A</sub>
CsVBr <sub>3</sub>	295.5	1,670
	265.5	1,731
	229.5	1,770
	197.4	1,857
	166.5	1,947
	135.3	2,087
	104.0	2,242
	89.5	2,328

**1. Anilinium tetrabromovanadate(II)**

Vanadium(II) bromide hexahydrate (2.30g.), dissolved in absolute ethanol (20cm<sup>3</sup>), was added to a solution of anilinium bromide (2.42g.) in ethanol (30cm<sup>3</sup>). The purple solution obtained was concentrated under vacuum until 25 cm<sup>3</sup> remained. 2,2-Dimethoxypropane (100cm<sup>3</sup>) was added with shaking. Light-grey crystals separated immediately from a light yellow solution. The crystals were filtered off, washed with ethanol containing a small amount of 2,2-dimethoxypropane and dried for two hours at room temperature, and at 120°C for a further eight hours under vacuum. The greyish orange compound was very air-sensitive and turned deep brown in 15 minutes in air.

**2. Ethylammonium tetrabromovanadate(II)**

Vanadium(II) bromide hexahydrate (1.93g), dissolved in ethanol (15cm<sup>3</sup>), was added to a solution of ethylammonium bromide (1.50g) in ethanol (20cm<sup>3</sup>). The purple solution obtained was concentrated under vacuum until 10cm<sup>3</sup> remained. 2,2-Dimethoxypropane (100cm<sup>3</sup>) was added with shaking. Yellowish brown crystals separated immediately from a light yellow solution. The crystals were filtered off, washed with ethanol and dried as in (1). The grey compound turned to violet and finally to brown in 10 minutes in air.

**3. Dimethylammonium tetrabromovanadate(II)**

Vanadium(II) bromide hexahydrate (2.82g), dissolved in ethanol (20cm<sup>3</sup>), was added to a solution of dimethylammonium bromide (2.0g) in

Table 3: Electronic spectral data ( $\text{cm}^{-1} \times 10^{-3}$ )

Compound	$\nu_3$	$\nu_2$	$\nu_1$	B	$\nu_3-\nu_2$ calc.	$\nu_3-\nu_2$ obs.	Calculated band positions		
							$\nu_3$	$\nu_2$	
[NPhH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	23.9m	20.4sh	12.8m	7.0s,vb	0.81	9.4	7.6	21.2	11.7
[NEtH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	23.9m	19.8s	12.3m	7.4s,vb	0.66	6.9	7.5	19.5	12.5
[NMe <sub>2</sub> H <sub>2</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	23.4s	20.2w	12.7w	7.2m	0.75	9.04	7.5	20.9	11.9
[n-C <sub>8</sub> H <sub>17</sub> NH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	23.0w	20.4sh	12.6m	7.6s,vb	0.68	7.4	6.8	20.7	12.8
[H <sub>2</sub> pipz] <sub>2</sub> [VBr <sub>6</sub> ]	23.6vw	20.0sh	12.3m	7.0m	0.75	9.0	8.1	20.6	11.6
[C(NH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	26.6sh	20.5sh	12.6vw	7.8w	0.64	8.0	7.9	20.54	12.5
CsVBr <sub>3</sub>	24.3m	20.0m	13.0m	7.4	0.75	9.05	7.0	21.27	12.2

Table 4: Far Infra-Red spectra (200-500  $\text{cm}^{-1}$ ) of vanadium (II) complex bromides

Compound	$\nu$ (V-Br)				
[NPhH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	500w,	455m,	382vw	352vw	210s
[NEtH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]		450w,	380vw,		220s
[NMe <sub>2</sub> H <sub>2</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]		450w,	390m,		225m
[n-C <sub>8</sub> H <sub>17</sub> NH <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]	465w,	450w,	390w,		225m
[H <sub>2</sub> pipz] <sub>2</sub> [VBr <sub>6</sub> ]				280s	220w
[C(NH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> [VBr <sub>4</sub> ]			405w,		225m
CsVBr <sub>3</sub>			390w sh,	310vw	240s, 210vw

ethanol. The purple solution obtained was concentrated under vacuum until 15  $\text{cm}^3$  remained. 2,2-Dimethoxypropane (100 $\text{cm}^3$ ) was added with shaking. Light violet crystals separated immediately from a light yellow solution. The crystals were filtered off, washed with ethanol and dried as in (1). The Khaki compound turned to deep brown in 10 minutes in air.

#### 4. n-Octylammonium tetrabromovanadate(II)

Vanadium(II) bromide hexahydrate (1.61g), dissolved in absolute ethanol (20 $\text{cm}^3$ ), was added to a solution of n-octylammonium bromide (2.08g) in ethanol (25 $\text{cm}^3$ ). The purple solution obtained was

concentrated under vacuum until 20 $\text{cm}^3$  remained. 2,2-Dimethoxypropane (100 $\text{cm}^3$ ) was added with shaking. Light violet crystals separated immediately from a light yellow solution. The crystals were filtered off, washed with ethanol and dried as in (1). The pale grey compound turned to brown in 15 minutes in air.

#### 5. Bis(piperazinium) hexabromovanadate(II)

Vanadium(II) bromide hexahydrate (4.15g), dissolved in 0.1M hydrobromic acid (20 $\text{cm}^3$ ), was added to a solution of piperazinium bromide (3.24g) in 0.1M hydrobromic acid (15 $\text{cm}^3$ ). The blue solution obtained was evaporated to dryness at

50°C by vacuum distillation to give a light yellow solid which was shaken with cold ethyl acetate, filtered off, washed with cold ethyl acetate and dried as in (1). The light yellow compound turned to brown in 10 minutes in air.

#### 6. Guanidinium tetrabromovanadate(II)

Vanadium(II) bromide hexahydrate (4.46g), dissolved in absolute ethanol (20cm<sup>3</sup>), was added to a solution of guanidinium bromide (3.62g) in ethanol (25cm<sup>3</sup>). The purple solution obtained was concentrated under vacuum until 15cm<sup>3</sup> remained. 2,2-Dimethoxypropane (100cm<sup>3</sup>) was added with shaking. Pale grey crystals separated immediately from a light yellow solution. The crystals were filtered off, washed with ethanol and dried as in (1). The grey compound turned to brown less than 5 minutes in air.

#### 7. Caesium tribromovanadate(II)

Vanadium(II) bromide hexahydrate (5.46g), dissolved in 0.1M hydrobromic acid (20cm<sup>3</sup>) was added to a solution of caesium bromide (3.61g), in 0.1M hydrobromic acid (25cm<sup>3</sup>). The blue solution obtained was evaporated to dryness at 50°C by

vacuum distillation to give a light grey compound which was shaken with cold ethyl acetate, filtered off, washed with cold ethyl acetate, and dried as in (1). The light brown compound turned to brown in 20 minutes in air.

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