# Mixed-valence Complexes of Vanadium with 1,10-Phenanthroline and 2,2′-Bipyridine

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The electronic structures of some intense purple vanadium complexes, initially formulated as $[L_2V^{III}(OH)_2V^{III}L_2]^{4+}$ [L = 1,10-phenanthroline(phen) or 2,2′-bipyridine(bipy)] have been investigated. The complexes were isolated as the sulphate or mixed hexafluorophosphate–chloride salts. Electronic spectra and magnetic and e.s.r. measurements show that the complexes are novel examples of binuclear mixed-valence species, containing vanadium in the oxidation states II and III bridged, probably, by a hydroxo-group. Characteristic visible bands of high intensity were observed at 16 000 and 19 000 cm$^{-1}$ and arise because of intervalence electron transfer. Vanadium $2p_{3/2}$ and $3p$ binding energies, obtained from $X$-ray photoelectron spectra, are characteristic of oxidation states of III and below. Individual bands due to more than one oxidation state of vanadium could not be detected with certainty, though some broadening was observed.

Although there has been much recent interest in binuclear oxo- and hydroxo-bridged 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) complexes of $Cr^{III}$,[1,2] $Mn^{III}$,[3] and $Fe^{III}$,[4] little is known of related species of $V^{III}$. Brandt *et al.*[5] briefly mentioned the isolation of a purple-black complex, from the reaction of aqueous vanadium(III) with phen, formulated as $[V_2(phen)_4(OH)_2]^{4+}$. Hydrolysis of $[VCl_2(phen)_2]Cl$ is also known to yield an intermediate purple-black derivative.[6] As part of a study of the electronic structures of polynuclear vanadium(III) complexes, we have investigated the spectral and magnetic properties of these proposed binuclear hydroxo-complexes. Most of our work has been carried out on solid samples. We hope to show in the results presented here that the complexes are novel examples of mixed-valency species. Indirect confirmation of this conclusion [7] has recently appeared in the $X$-ray structure determination [3] of a related di-μ-oxo-manganese derivative $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2](ClO_4)_3,3H_2O$.

## RESULTS AND DISCUSSION

*Synthesis and Properties.*—Vanadium(III) alum reacted with ligand [L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)] in a small volume of water to give initially a dark red-brown solution which quickly turned deep purple-black. Microcrystalline aggregates or powdered solid complexes were deposited on setting aside these solutions; it was not possible to obtain single crystals. Analyses of the complexes showed a V : L : $SO_4^{2-}$ ratio of 1 : 2 : 1 and a variable degree of hydration. Thus, using, initially, the stoicheiometry $VL_2(OH)(SO_4),nH_2O$, we found that $n$ can vary between preparations, *i.e.* for L = phen, $n$ = 4, 5, or 5·5 and for L = bipy, $n$ = 4, 5·5, or 7. The tetrahydrates were generally obtained. Attempts to prepare the $PF_6^-$ salt, starting from $VCl_3,6H_2O$, gave the mixed-anionic species $VL_2(OH)(PF_6)_{1\cdot3}Cl_{0\cdot7}$; samples of this stoicheiometry could be reproducibly prepared. Preliminary studies showed that $ClO_4^-$ and $BF_4^-$ derivatives could also be precipitated, but these were not studied further.

The solid complexes are stable in air but change slowly in solution to green $[VOL_2]^{2+}$ species. The sulphate complexes are non-conducting in methanol, and an approximate molecular-weight measurement in this solvent gave a value corresponding to twice that of the monomeric formulation. The mixed hexafluorophosphate–chloride complexes are highly ionized in acetone, showing conductance values in the approximate range of 1 : 2 to 1 : 3 electrolytes. It was not possible to carry out oxidation-state titrations on the complexes because of simultaneous oxidation of the organic ligands.

Mull i.r. spectra of the $VL_2(OH)(SO_4),nH_2O$ complexes showed bands due to lattice $H_2O$ at *ca.* 3350 cm$^{-1}$. Co-ordinated bipy bands were observed at 1599 and 1560 cm$^{-1}$, similar positions have recently been observed [8] for $[V(bipy)_3]I_2$. Vanadium–nitrogen stretching frequencies were observed in all the present complexes at *ca.* 380 cm$^{-1}$, in accord with the recent findings of Saito *et al.*[8] for tris chelate complexes of vanadium. I.r. spectra of the sulphate complexes showed bands due to co-ordinated $SO_4$ at 1132, 1032, and 982 cm$^{-1}$.

*Electronic Spectra.*—Band positions in the u.v.–visible spectra of the complexes are shown in Table 1. The solid and solution spectra were very similar. The two intense u.v. bands at *ca.* 43 000 and *ca.* 35 000 cm$^{-1}$ are characteristic of chelated phen or bipy and are due to internal ligand ($\pi \longrightarrow \pi^*$) transitions.[9] The visible region is characterized by two intense, closely spaced bands at *ca.* 16 000 and 19 000 cm$^{-1}$ (Figure 1) (there is possibly a shoulder at 21 000 cm$^{-1}$). The intensities of these bands are much higher than those normally expected for *d–d* transitions arising from octahedral chromophores of $V^{II}$, $V^{III}$, or $V^{IV}$. High-intensity bands in the visible region can, in general, arise for a number of reasons. (*a*)

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Charge transfer between metal and ligand orbitals relaxes the Laporte rule. This mechanism has been discussed recently in some detail.[9,10] It occurs particularly in monomeric tris chelate complexes such as $[V(bipy)_3]^{2+}$ (Table 2); the latter complex has an intense purple-black colour,[11] very similar to that of the present complexes. (*b*) Enhanced intensities can arise between pairs of metal ions in the same oxidation state due to an exchange-induced mechanism.[12] Oxo-bridged species generally show higher intensity bands than di-hydroxo-bridged species, *e.g.* $[Cr^{III}(phen)_2]_2O^{4+}$ (ref. 1). The spin-allowed bands in the spectra of these complexes generally appear in the same position as those of the analogous single-ion centre. (*c*) Electron transfer between adjacent metal ions in two different oxidation states can also give rise to intense bands[13-15] (termed ' intervalence ' or ' mixed-valence ' charge transfer). In these complexes the mixed-valence transition generally occurs at a different position to that of the visible bands of the constituent ions. The order of intensities due to the above three mechanisms is in the order $(a) \sim (c) \gg (b)$.

The positions of the bands in the present complexes are too close together to allow any reasonable fit to octahedral *d–d* energy levels arising from just one of the oxidation states II, III, and IV of vanadium. Band positions, intensities, and assignments for a number of related phen and bipy complexes of vanadium are given in Table 2. The spectra of the present complexes differ from all these. The overall evidence, from

TABLE 1

Electronic spectra ($10^{-3}\bar{\nu}/cm^{-1}$) of vanadium phen and bipy complexes and related systems ($\varepsilon_{max.}/l\ mol^{-1}\ cm^{-1}$ in parentheses)

| Compound | Phase | Intervalence electron transfer | | | Intraligand ($\pi \longrightarrow \pi^*$) (1) | Intraligand ($\pi \longrightarrow \pi^*$) (2) |
|---|---|---|---|---|---|---|
| phen | $H_2O$ | | | | 37·8 | 44·0br |
| $V(phen)_2(OH)(SO_4)$ | $H_2O$ | 16·2 | 19·2 | (21·0sh) | 36·5 | 44·5 |
| | MeOH | 15·3 | 19·0 | (21·4sh) | 36·5 | 44·5 |
| | | (1000) | (1000) | | | |
| | Refl. | 15·2 | 18·2 | | 37·4 | 45·0 |
| $V(phen)_2(OH)(PF_6)_{1·3}Cl_{0·7}$ | $H_2O$ | 16·2 | 19·3 | | 37·0 | 44·5 |
| | MeOH | 15·2 | 19·2 | | | |
| | $Me_2CO$ | 15·2 | 18·2 | | | |
| | | (2000) | (2000) | | | |
| bipy | $H_2O$ | | | | 35·6 | 42·8 |
| $V(bipy)_2(OH)(SO_4)$ | $H_2O$ | 16·1 | 19·1 | | 33·8 | 42·2 |
| | MeOH | 15·3 | 19·2 | | | |
| | | (1200) | (1200) | | | |
| | Refl. | 15·0 | 16·7sh | | 34·3 | 42·2 |
| $V(bipy)_2(OH)(PF_6)_{1·3}Cl_{0·7}$ | $H_2O$ | 16·2 | 19·2 | | 34·0 | 42·2 |
| | MeOH | 15·3 | 18·6 | | | |
| | $Me_2CO$ | 15·1 | 18·1 | | | |
| | | (2500) | (2500) | | | |
| Vanadium(III) alum + terpy (purple) | $H_2O$ | 14·7 | 19·5sh | 21·4 | 35·4 | 50·2 |
| Vanadium(III)–terpy dimer (red) [a] | $H_2O$ | 14·6 | 18·5sh | 21·1 | | |
| $K_{3·5}V(CN)_{5·5}(OH)_{0·5}$ [b] | aq. KCN | 17·0 | | | | |
| | | (2000) | | | | |

[a] Ref. 21. [b] Ref. 18.

TABLE 2

Visible spectra of phen and bipy complexes with vanadium in various oxidation states

| Oxidation state | Complex | Colour | Band positions ($cm^{-1}$) and intensities ($\varepsilon_{max.}$) | Assignments | Ref. |
|---|---|---|---|---|---|
| Mixed ? | $[VL_2OH]^{2+}$ | Purple-black | *ca.* 16 000 (2000) | Intervalence | This work |
| | L = phen and bipy | | *ca.* 19 000 (2000) | | |
| II | $[V(bipy)_3]^{2+}$ | Purple-black | 16 150 (4500) [a] | $^4A_{2g} \longrightarrow {}^4T_{2g}$ + c.t. | 11 |
| | | | 25 050 (2650) [a] | $^4A_{2g} \longrightarrow {}^4T_{1g}$ + c.t. | |
| III | $[V(bipy)_2Cl_2]^+$<br>$[V(phen)_2Cl_2]^+$ | Yellow | 14 500 (40) | $^3T_{1g} \longrightarrow {}^3T_{2g}$ | 6 |
| | | | 20 000sh | $^3T_{1g} \longrightarrow {}^3T_{1g}(P)$ | |
| IV | $[VO(phen)_2]^{2+}$ | Yellow-brown | 16 000 | $^2B_2 \longrightarrow {}^2B_1$ | *b* |
| | | | 23 000 | $^2B_2 \longrightarrow {}^2A_1$ | |
| | $[VOCl_2(bipy)]$ | Green | 13 300 (39) | $^2B_2 \longrightarrow {}^2E$ | *b* |
| | | | 16 000 (25) | $^2B_2 \longrightarrow {}^2B_1$ | |
| | | | 26 800 (500) | $^2B_2 \longrightarrow {}^2A_1$ | |
| | $VCl_4(bipy)$<br>$VCl_4(phen)$ | Brown | 17 400 [c] | $^2B_2 \longrightarrow {}^2B_1$ | *b* |
| | | | 21 300 [c] | $^2B_2 \longrightarrow {}^2A_1$ | |

[a] Bands show vibrational structure. [b] J. Selbin, *Chem. Rev.*, 1965, **65**, 153. [c] These bands form a broad asymmetric doublet at *ca.* 19 000 $cm^{-1}$.

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[10] C. K. Jorgenson, *Progr. Inorg. Chem.*, 1970, **12**, 101; J. E. Fergusson and G. M. Harris, *J. Chem. Soc.* (*A*), 1966, 1293.

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[12] J. Ferguson, *Progr. Inorg. Chem.*, 1970, **12**, 159.

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[14] P. Day, *Inorg. Chim. Acta, Rev.*, 1969, **3**, 81.

[15] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.

position and intensity arguments, suggests that mechanism (*c*) is operating, *i.e.* there is electron transfer between two different oxidation states of vanadium. Magnetic and e.s.r. properties, discussed below, can only be interpreted assuming the presence of $V^{II}$, which, together with spectral similarities, confirms that one oxidation state in these complexes must be II. It is difficult from spectra alone to distinguish the other oxidation state between those of III and IV. The close spacing of the two bands is possibly due to electron transfer to a distorted octahedral centre. Complexes of both $V^{III}$ and $V^{IV}$ are known to have *T* terms split to this magnitude.[16,17]

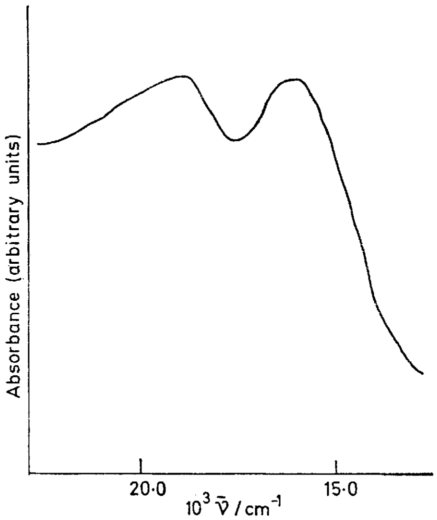

FIGURE 1 Visible spectrum of $V(phen)_2(OH)(SO_4)$ in $H_2O$: $\varepsilon_{max.}$ *ca.* 1000 l mol$^{-1}$ cm$^{-1}$

Indirect evidence for the mixed-valence assignment is obtained by a comparison with spectra of other proposed mixed-valence vanadium complexes. Thus Bennett and Nicholls[18] observed an intense band at 17 000 cm$^{-1}$ for the purple-black complex $[(CN)_6V^{II}(OH)V^{III}(CN)_5]^{7-}$, and Robin and Day[13] suggested that the intense band at 23 500 cm$^{-1}$ in hydrolysed $V^{III}$ solutions could be due to $[V^{II}–O–V^{IV}]^{4+}$ rather than to $[V^{III}(OH)_2V^{III}]^{4+}$ or $[V^{III}OV^{III}]^{4+}$ (refs. 19 and 20). Furthermore, Bennett and Taube[21] have prepared a red vanadium(III)–2,2′,2″-terpyridine species, in aqueous solution (pH 3·5), with similar spectral characteristics to those of the present complexes, and, by analogy with Brandt's[5] work, have proposed the structure $[(terpy)V^{III}(OH)_2V^{III}(terpy)]^{4+}$. They noted that under certain conditions this complex disproportionated to $[V^{II}(terpy)_2]^{2+}$ and $[V^{IV}(terpy)]^{4+}$. It is perhaps noteworthy that a mixed-valence complex of tungsten,[22] $[Cl_5W^{III}–O–W^{V}Cl_5]^{4-}$, is deep purple and has an intense band at 19 500 cm$^{-1}$.

*Magnetic Properties.*—Except in one case, magnetic moments (per vanadium ion) of the solid complexes lie within the range 3·3 ± 0·2 B.M. and show Curie–Weiss behaviour over the range 300—90 K, the θ values being small (Table 3). The $\mu_{eff}$ values are too high to arise from vanadium(III) centres alone, since previous measurements on monomeric or polymeric species have shown[23] values of $<$ *ca.* 2·9 B.M. The moments lie between those expected for $V^{III}$ and $V^{II}$. If we assume dimeric moieties with zero exchange interactions, then the calculated moments are $\mu = 3{\cdot}39$ B.M. for $[V^{II}, V^{III}]$ and $\mu = 3{\cdot}0$ B.M. for $[V^{II}, V^{IV}]$. Antiferromagnetic exchange interactions could decrease such room-temperature values, whilst ferromagnetic exchange could give small increases. The small positive θ values are indicative, at least in the 300—90 K range, of little or no antiferromagnetic exchange interaction. Weak interactions have been observed[2,24] in the hydroxo-species $[L_2Cr(OH)]_2^{4+}$ and $[LCu(OH)]_2^{2+}$, whilst strong interactions were found in the oxo-species $[L_2Cr]_2O^{4+}$ (ref. 1), $[L_2Fe]_2O^{4+}$ (ref. 4), and $[L_4Mn^{III}Mn^{IV}(O)_2]^{3+}$ (L = phen or bipy) (ref. 3).

Some magnetic measurements have previously been made on other proposed mixed-valence vanadium complexes; thus $\mu_{eff} = 3{\cdot}4$ B.M. was found[18] for $[(CN)_6V^{II}(OH)V^{III}(CN)_5]^{7-}$ and $\mu_{eff} = 3{\cdot}35$ B.M. ($\theta = 18°$) for[25] $V^{II}V^{III}F_5,7H_2O$.

TABLE 3

Magnetic properties

| Complex | | $\mu_{eff}$ (293 K) / B.M. | θ / K |
|---|---|---|---|
| $V(phen)_2(OH)(SO_4),4H_2O$ | Sample 1 | 3·64 | 25 |
| | Sample 2 | 3·40 | |
| $V(phen)_2(OH)(SO_4),5H_2O$ | | 3·46 | |
| $V(phen)_2(OH)(SO_4)(5{\cdot}5H_2O$ | | 3·61 | 23 |
| $V(phen)_2(OH)(SO_4),6H_2O$ | | 3·59 | 24 |
| $V(bipy)_2(OH)(SO_4),5{\cdot}5H_2O$ | | 3·36 | 21 |
| $V(bipy)_2(OH)(SO_4),7H_2O$ | | 3·47 | |
| $V(phen)_2(OH)(PF_6)_{1{\cdot}3}Cl_{0{\cdot}7}$ | | 3·62 | |
| $V(bipy)_2(OH)(PF_6)_{1{\cdot}3}Cl_{0{\cdot}7}$ | | 2·75 | 16 |
| $K_7[(CN)_6V^{II}(OH)V^{III}(CN)_5]$ [a] | | 3·4 ± 0·2 | |
| $V^{II}V^{III}F_5,7H_2O$ [b] | | 3·35 | 18 |

[a] Ref. 12. [b] Ref. 17.

*E.s.r. Spectra.*—The e.s.r. spectrum of powdered $V(phen)_2(OH)(SO_4),4H_2O$ is given in Figure 2 and shows a very broad line with a sharp inflection at *ca.* 3000 G. The spectrum of the vanadium(II) complex $[V(bipy)_3]I_2$ was also recorded and is given in Figure 3; it has been described briefly previously[26] and has very similar characteristics to those of $V(phen)_2(OH)(SO_4),4H_2O$.

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[16] D. J. Machin and K. S. Murray, *J. Chem. Soc.* (*A*), 1967, 1330.

[17] D. J. Machin and K. S. Murray, *J. Chem. Soc.* (*A*), 1967, 1498.

[18] B. G. Bennett and D. Nicholls, *J. Chem. Soc.* (*A*), 1971, 1204.

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[21] L. E. Bennett and H. Taube, *Inorg. Chem.*, 1968, **7**, 254.

[22] E. König, *Inorg. Chem.*, 1969, **8**, 1278.

[23] E. König, Landolt–Börnstein Tables, Group II, vol. 2 (Springer Verlag 1966).

[24] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 904.

[25] H. J. Seifert, H. W. Loh, and K. Jungnickel, *Z. anorg. Chem.*, 1968, **360**, 62.

[26] E. König, H. Fischer, and S. Herzog, *Z. Naturforsch.*, 1963, *B***18**, 432.

Spectra were also measured on methanolic glass samples and again they are very similar (Figures 4 and 5), but with better resolution in the 3000 G region, where $^{51}V$ hyperfine structure is observed. These results, like the magnetic-susceptibility studies, show that the present complexes contain vanadium in the II oxidation state. The spectra also give reasonably clear evidence that the other oxidation state is III, since vanadium(III) complexes do not show any *X*-band resonances and the spectra can be fully explained in terms of vanadium(II). Great care was taken to exclude any oxygen or moisture from all the e.s.r. samples and we feel confident that no oxidation to vanadium(IV) occurred.

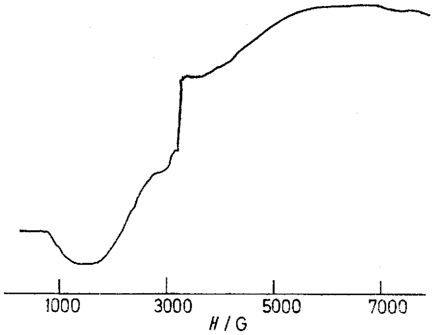

FIGURE 2 E.s.r. spectrum of solid $V(phen)_2(OH)(SO_4),4H_2O$ at 77 K: microwave frequency 9081 MHz

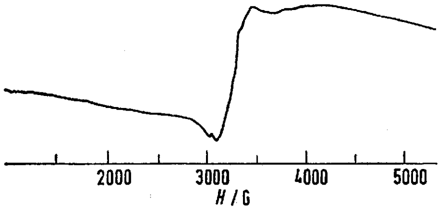

FIGURE 3 E.s.r. spectrum of solid $[V(bipy)_3]I_2$ at 77 K: microwave frequency 9084 MHz

*X-Ray Photoelectron Spectra.*—Vanadium $2p_{3/2}$ and $3p$ electron binding energies were obtained [27] for two of the present complexes and a number of other vanadium complexes with oxidation states II, III, IV, and V (Table 4). Despite the complexity and size of the present complexes, it was hoped that bands due to more than one oxidation state of vanadium might be simultaneously observed.

Since there are few previous reports [28] of *X*-ray photoelectron spectra of vanadium complexes, it is appropriate to briefly describe some general aspects of the spectra obtained. The vanadium $2p_{3/2}$ line occurs close to the oxygen $1s$ line but can be clearly distinguished. The $2p_{3/2}$ and $3p$ lines in the diamagnetic $V^V$ complexes are narrower than those in the paramagnetic $V^{IV}$, $V^{III}$, and $V^{II}$ derivatives, the broadness in the latter being due to interactions with the valence *d* electrons.[29] In general, the $3p$ line was found to be weaker and more asymmetric than the $2p_{3/2}$ line. It is difficult to obtain accurate linewidths and positions for such asymmetric bands; values in Table 4 correspond to the position of the top of the peak. Other vanadium lines such as $2p_{1/2}$, $2s$, and $3s$ are very weak and in some cases obscured by oxygen and copper lines (from sample support).

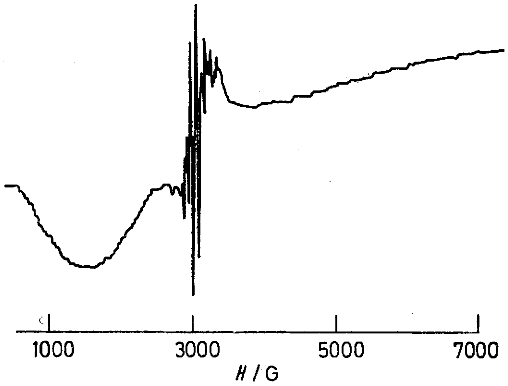

FIGURE 4 E.s.r. spectrum of $V(phen)_2(OH)(SO_4),4H_2O$ in methanol glass (77 K): microwave frequency 9081 MHz

The results in Table 4 show that the shift of the $2p_{3/2}$ line is virtually independent of oxidation state, except perhaps for a small decrease in going from $V^{III}$ to $V^{II}$, whilst a small but discernible decrease with lowering of oxidation state is shown by the $3p$ line. Similar trends have previously been observed in other first-row transition-metal complexes.[30-32] The spectra of the $VL_2(OH)SO_4$ complexes show $2p_{3/2}$ and $3p$ lines which are somewhat weaker than those in the other complexes. It is not possible to distinguish two separate lines for each level which might be expected in a mixed-valence system. The broadness of the lines can be explained in terms of the paramagnetic effect, described above. A weak tail (or shoulder) is shown on the low-energy side of the $2p_{3/2}$ lines for these two complexes, but cannot readily be

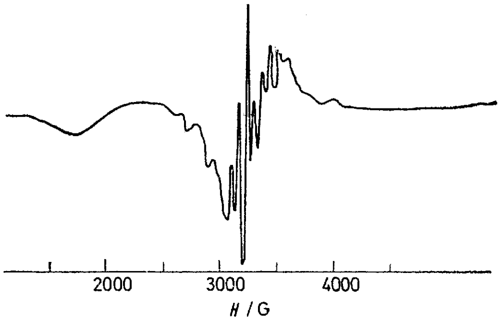

FIGURE 5 E.s.r. spectrum of $[V(bipy)_3]I_2$ in methanol glass (77 K): microwave frequency 9084 MHz

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[27] R. D. Brown and D. McGavin, unpublished results.

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[30] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 1970, **9**, 612.

[31] L. N. Kramer and M. P. Klein, *J. Chem. Phys.*, 1969, **51**, 3618.

[32] J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, 1972, **57**, 973.

assigned to a different oxidation state as was the case in the better resolved $2p_{3/2}$ spectra of Prussian Blue[33] and bis(ferrocene) $Fe^{II}Fe^{III}$ picrate.[34] The $2p_{3/2}$ and $3p$ shifts are more dependent on oxidation state in iron complexes. The present results are not in disagreement with a mixed-valence structure since quite small differences in line positions would be expected.*

The results are certainly indicative of the presence of lower oxidation states of vanadium and $3p$ energies would rule out any state higher than that of III; this is in accord with the spectral and magnetic studies. A full account of the $X$-ray photoelectron studies on the vanadium complexes, including theoretical calculations, will be given later.[27]

TABLE 4

Vanadium $2p_{3/2}$ and $3p$ binding energies (eV) and linewidths (eV)

| Oxidation state and $d^n$ configuration | Compound | $2p_{3/2}$ | | $3p$ | |
|---|---|---|---|---|---|
| | | Binding energy [a] | Line width [b] | Binding energy [a] | Line width [b] |
| $V^V(d^0)$ | $V_2O_5$ | 515·9 | 1·4 | 41·2 | 2·5 |
| | $NH_4VO_3$ | 515·7 | 2·0 | 41·4 | 3·0 |
| $V^{IV}(d^1)$ | $VOSO_4$ | 516·1 | 1·9 | 40·8* | 3·9 |
| | $[VO(phen)_2]SO_4$ | 515·1 | 2·2 | 40·3* | 4·8 |
| | $[VO(bipy)_2]SO_4$ | 515·8 | 2·1 | 40·8* | 4·8 |
| $V^{III}(d^2)$ | $(NH_4)V(SO_4)_2,12H_2O$ | Decomposed on irradiation | | | |
| | $VCl_3$ | 515·3 | 2·5 | 40·1* | 4·4 |
| $V^{II}(d^3)$ | $[V(bipy)_3]I_2$ | 514·5—512·5 [c] | 3·6 | 37·6 | 4·4 |
| Mixed | $V(phen)_2(OH)SO_4$ | 512·7 | 4·0 | 38·1* | 6·0 |
| | $V(bipy)_2(OH)SO_4$ | 514·4 | 2·2 | 39·3* | 4·6 |

[a] *Ca.* ±0·3 eV. [b] Linewidths taken at half-height; error *ca.* ±0·1 eV except in the cases marked with an asterisk, where it is *ca.* ±0·5 eV. The energies of the latter asymmetric bands were taken at the top of the peak. [c] Very broad line.

## CONCLUSIONS

The results presented above certainly suggest the formation of mixed-valency vanadium di-imine complexes. A binuclear structure with hydroxo-bridging between $V^{II}$ and $V^{III}$ centres is consistent with the spectral and magnetic measurements. The stoicheiometry $[VL_2OH]^{2+}$ has been used throughout and this cannot be distinguished analytically from that required by $[VL_2(OH)_{0\cdot5}]^{2\cdot5+}$. The following structures are possible: (i) $[L_2(SO_4)V^{II}\text{–}OH\text{–}V^{III}L_2(SO_4)]$, involving six-co-ordinate vanadium, unidentate $SO_4$, and a single hydroxo-bridge similar to that proposed by Nicholls[18] for the $V^{II,III}$ cyano-complex; (ii) $[L_2V^{II}\text{–}OH\text{–}V^{III}L_2][(PF_6)_{2\cdot6}Cl_{1\cdot4}]$, involving five-co-ordinate vanadium *or* $[L_2V^{II}(OH)(Cl)V^{III}L_2][(PF_6)_{2\cdot6}Cl_{0\cdot4}]$, involving six-co-ordinate vanadium and a mixed bridge.

Broad-line n.m.r. spectra were also recorded to see if it was possible to simultaneously observed $^{51}V$ resonances due to the different oxidation states. However the present complexes, and a number of known monomeric complexes in oxidation states II, III, and IV, all showed one broad resonance in exactly the same position (6·903 kG at radio frequency 7·6596 MHz). If there are any small shift differences then they are presumably hidden within this broad line.

## EXPERIMENTAL

Vanadium(III) alum, $(NH_4)V(SO_4)_2,12H_2O$,[35] and $VCl_3,6H_2O$[36] were prepared using conventional electrochemical techniques with a lead anode and a mercury cathode. Vanadium was analysed using permanganate titrations. Sulphate ions were determined gravimetrically with barium chloride.

*Reaction of Vanadium*(III) *Alum with* 1,10-*Phenanthroline*-(*phen*).—Two related sets of reaction conditions were used, differing mainly in dilution.

(i) The alum (1·2 g, 2·5 mmol) was dissolved in hot water (1 $cm^3$) to yield a green-brown solution. 1,10-Phenanthroline hydrate (1·0 g, 5 mmol) was then added and an intense purple solution developed immediately. On warming, and subsequent cooling, a dark purple product was precipitated. The product was washed with water, ethanol, and acetone and dried *in vacuo*. Different preparations (*a*)—(*d*) yielded complexes $V(phen)(OH)(SO_4),nH_2O$, where $n$, the degree of hydration, varied from 4 to 6 [(*a*) Found: C, 48·1; H, 4·1; N, 9·3; S, 5·6; $SO_4$, 16·9. $V(phen)_2(OH)(SO_4),4H_2O$ requires C, 48·3; H, 4·2; N, 9·4; S, 5·4; $SO_4$, 16·1. (*b*) Found: C, 46·1; H, 4·2; N, 9·2; S, 6·0. $V(phen)_2(OH)(SO_4),5H_2O$ requires C, 46·9; H, 4·4; N, 9·1; S, 5·2. (*c*) Found: C, 46·1; H, 4·0; N, 8·9; S, 4·9; V, 9·6. $V(phen)_2(OH)(SO_4),5\cdot5H_2O$ requires C, 46·2; H, 4·5; N, 9·0; S, 5·1; V, 8·9. (*d*) Found: C, 45·0; H, 4·1; N, 8·8; S, 4·5. $V(phen)_2(OH)(SO_4),6H_2O$ requires C, 45·6; H, 4·6; N, 8·8; S, 5·0%].

(ii) The alum (1·9 g) was dissolved in water (10 $cm^3$) and to it was added a suspension of phen (1·6 g) in water (10 $cm^3$). Initially a dark red-brown colour developed which rapidly changed to deep purple. On being set aside at 0 °C overnight, a purple-black microcrystalline product was precipitated, which was washed with water and dried over conc. $H_2SO_4$. The analysis corresponded to the tetrahydrate [Found: C, 47·8; H, 4·4; N, 9·3; S, 5·6; V, 8·9%. $\nu$ 3350m(br), 1640m, 1620m, 1605w, 1580m, 1512m, 1428m, 1341m, 1302w, 1168sh, 1151m, 1132s ($SO_4$), 1104sh, 1055sh,

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* *Note added in proof:* Two distinct $V(2p_{3/2})$ lines at 515·3 and 512·6 eV are observed for the complex $K_a[(CN)_6V^{II}OHV^{III}(CN)_5]$ in agreement with the results in Table 4.

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1040s, 1030s ($SO_4$), 992s, 982s ($SO_4$), 971sh, 870m, 851s, 812w, 725s, 648m ($SO_4$), 635w, 604m ($SO_4$), 559w, 506w, 455w, 440w, 429m ($SO_4$), 375m, 360sh, 325m, 320m, 304w, 285w, and 275w; ν(V–N) 375 $cm^{-1}$; $\lambda_m$ (per dimer in MeOH) 10 $\Omega^{-1}$ $cm^2$ $mol^{-1}$; *M* (in MeOH) *ca.* 1200].

*Reaction of Vanadium*(III) *Alum with* 2,2′-*Bipyridine* (*bipy*).—Similar reaction conditions to those for phen were used. Hydrates of $n = 4$, 5·5, and 7 were obtained [(*a*) Found: C, 43·3; H, 4·4; N, 10·3; S, 5·6; $SO_4$, 17·5; V, 9·9. $V(bipy)_2(OH)(SO_4),4H_2O$ requires C, 43·8; H, 4·6; N, 10·2; S, 5·8; $SO_4$, 17·5; V, 9·3. (*b*) Found: C, 41·7; H, 4·9; N, 9·6; S, 5·5. $V(bipy)_2(OH)(SO_4),5{\cdot}5H_2O$ requires C, 41·7; H, 4·9; N, 9·7; S, 5·6. (*c*) Found: C, 39·4; H, 3·7; N, 9·3; S, 5·6. $V(bipy)_2(OH)(SO_4),7H_2O$ requires C, 39·8; H, 5·2; N, 9·3; S, 5·3%. ν 3350s,br, 1640m, 1605sh, 1599m, 1560w, 1491w, 1442m, 1315m, 1283w, 1244w, 1221w, 1171sh, 1160sh, 1145s, 1132s ($SO_4$), 1111sh, 1060sh, 1042s, 1038sh, 1020s ($SO_4$), 961s ($SO_4$), 809w, 768s, 730s, 717sh, 655m, 645m ($SO_4$), 600m ($SO_4$), 464w, 441m, 419m ($SO_4$), 408sh, and 384s; ν(V–N) 384 $cm^{-1}$; $\lambda_M$ (per dimer in MeOH) 15 $\Omega^{-1}$ $cm^2$ $mol^{-1}$].

*Reaction of Trichlorovanadium*(III) *Hexahydrate with* 1,10-*Phenanthroline and Potassium Hexafluorophosphate*.—1,10-Phenanthroline (0·6 g, 3·03 mmol) was added to a solution of $VCl_3,6H_2O$ (0·4 g, 1·52 mmol) dissolved in water (1 $cm^3$). $KPF_6$ (1·0 g, 5·44 mmol) in hot water (5 $cm^3$) was then added to the resulting purple solution. After warming, and subsequent cooling, the purple product was precipitated. It was washed with hot water and ethanol and dried *in vacuo* [Found: C, 44·2; H, 3·0; Cl, 3·8; F, 24·2; N, 8·6. $V(phen)_2(OH)(PF_6)_{1\cdot3}Cl_{0\cdot7}$ requires C, 44·9; H, 2·7; Cl, 3·9; F, 23·1; N, 8·7%. ν(OH) 3220m, 3600m?; δ(OH) 978m; ν($PF_6$) 840vs and 560s; ν(V–N) 379 $cm^{-1}$; $\lambda_M$ (per dimer in acetone) 340 $\Omega^{-1}$ $cm^2$ $mol^{-1}$].

*Reaction of Trichlorovanadium*(III) *Hexahydrate with* 2,2′-*Bipyridine and Potassium Hexafluorophosphate*.—The same procedure was used as in the phen case [Found: C, 40·0; H, 3·1; Cl, 5·6; F, 25·9; N, 9·0; V, 8·2. $V(bipy)_2(OH)(PF_6)_{1\cdot3}Cl_{0\cdot7}$ requires C, 40·4; H, 2·9; Cl, 4·2; F, 25·0; N, 9·4; V, 8·7%. ν(OH) 3200m, 3250m, 3485m?, and 3620m?; δ(OH) 971m; ν(OD) 2460m; δ(OD) 745 $cm^{-1}$; ν($PF_6$) 840vs and 559vs; ν(V–N) 385 $cm^{-1}$].

*Reaction of Vanadium*(III) *Alum with* 2,2′,2″-*Terpyridine* (*terpy*).—A bright purple solution was formed when terpy was added to aqueous vanadium(III) alum. The complex was not further characterized. Its u.v.–visible spectrum was recorded.

*Tris*(2,2′-*bipyridine*)*vanadium*(III) *Tri-iodide*.—This complex was prepared using the method of Herzog [37] and characterized by its electronic spectrum in degassed methanol (15 400, 16 400sh, and 24 750 $cm^{-1}$).

Magnetic measurements were made at 14 temperatures over the range 300—90 K using the Gouy method. Electronic spectra were recorded on solutions using a Unicam SP 700 instrument, and on solids using a Beckman DK 2A spectrometer. *X*-Band e.s.r. spectra were recorded with a conventional spectrometer. Field strengths were calibrated using a proton probe. Samples were handled in a glove-box under rigorously anaerobic conditions. Broad-line n.m.r. spectra were recorded using a Varian 15 in Fieldial magnet system with a Varian R–F unit (model V4210 A) and a crystal-stabilizer locking device. Measurements were made on $[V(bipy)_3]I_2$, $V(acac)_3$ (acac = acetylacetonate), $V^{III}$ alum, $VOSO_4,H_2O$, $VO(acac)_2$, $NH_4VO_3$, $V_2O_5$, $V(phen)_2(OH)(SO_4)$, and $V(bipy)_2(OH)(PF_6)_{1\cdot3}Cl_{0\cdot7}$. The resolution was the same in both solid and solution phases. *X*-Ray photoelectron spectra were obtained using a commercial AEI ES100 *X*-ray photoelectron spectrometer with Al-$K_\alpha$ radiation of wavelength 1486·6 eV. Powdered samples were supported on a copper gauze. The line shifts were calibrated relative to the $2p_{3/2}$ line of copper at 931·0 ± 0·2 eV. Conductance measurements were made at room temperature using a Wayne–Kerr bridge. Molecular-weight measurements were made using a Mechrolab osmometer.

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