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Synthesis, magnetism, electrochemistry and reactivity of dinuclear vanadium(III) complexes of a macrocyclic tetraimine Schiff base †

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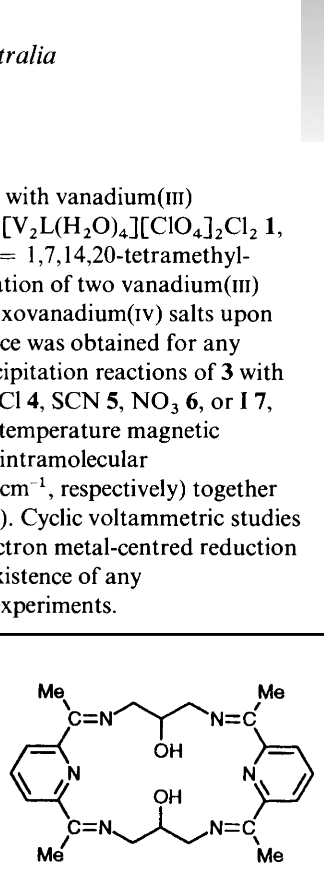
Transmetallation of the tetraimine Schiff-base complex $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ with vanadium(III) trichloride, vanadyl(IV) sulfate trihydrate or vanadyl(IV) dichloride dihydrate gave $[V_2L(H_2O)_4][ClO_4]_2Cl_2$ **1**, $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ **2** and $[V_2L(H_2O)_4][SO_4]_2{\cdot}H_2O$ **3**, respectively {H_2L = 1,7,14,20-tetramethyl-2,6,15,19-tetraaza[7.7](2,6)pyridinophane-1,6,14,19-tetraene-4,17-diol}. Incorporation of two vanadium(III) ions within the macrocyclic cavity also resulted from the template action of these oxovanadium(IV) salts upon 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol in refluxing methanol. No evidence was obtained for any vanadium(IV)-containing species having been produced en route. Metathetical precipitation reactions of **3** with various barium salts led to the isolation of $[V_2L(H_2O)_4][X]_4{\cdot}nH_2O$ species (X = Cl **4**, SCN **5**, NO_3 **6**, or I **7**, n = 2–8). These complexes exhibit reduced magnetic moments at 295 K. Variable-temperature magnetic susceptibility studies on representative powdered samples of **1** and **5** showed weak intramolecular antiferromagnetic coupling between the vanadium(III) centres ($J = -20$ and -25 cm^{-1}, respectively) together with a smaller intermolecular contribution ($\theta = -2.0$ and -3.7 cm^{-1}, respectively). Cyclic voltammetric studies on acetonitrile solutions of **2** revealed two waves attributable to sequential one-electron metal-centred reduction processes to yield $[V_2L]^{3+}$ and $[V_2L]^{2+}$ species. No evidence was found for the existence of any V^{IV}-containing species, through either electrochemical and/or chemical oxidation experiments.

Polyimine macrocyclic Schiff base, and their transition-metal complexes have been the subject of intense interest throughout recent years.[1] Of interest in the present study is the [2 + 2] macrocycle H_2L which forms on cyclocondensation of 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol.[2,3] It is prepared in high yield by a template reaction in the presence of Ba^{2+} and is versatile in its co-ordination behaviour, being found to form an array of metal complexes of differing geometry and nuclearity. When co-ordinated to manganese(II) the alkoxo O atoms provide intermolecular bridging between dinuclear entities to form tetranuclear 'pair-of-dimers' compounds.[4] Intermolecular bridging has also been furnished by chloro and azido entities to form similar manganese(II) tetranuclear compounds, of the type $[\{Mn_2(HL)X_2\}_2]^{2+}$ (X = Cl or N_3).[5] Dinuclear copper(II)[6] and iron(III)[7] compounds have also been formed, by transmetallation reactions of the barium complex. This compound has also been found to undergo an expansionary rearrangement in solution to form a [4 + 4] macrocycle incorporating a tetranuclear manganese(II) cubane-shaped core.[4,8]

Early transition-metal-ion complexes of this macrocycle have been less well explored. We recently reported a preliminary study of a vanadium(III) dinuclear complex including its crystal structure.[9] This work has been extended in the present study and new preparative routes have been developed which allow formation of a series of new dinuclear vanadium(III) macrocyclic complexes. The syntheses, magnetic, reactivity and electrochemical properties are now reported.

Interest in polynuclear vanadium species has been further fuelled by the recognition of the occurrence of vanadium in biomolecules such as algal haloperoxidases,[10] marine ascidians[11] and vanadium-containing nitrogenase enzymes.[12] To gain an insight into the fundamental chemistry involved within these complex systems it is useful to study low-molecular-weight dinuclear model compounds of the present type, in order to obtain structural, spectral, magnetic, redox and reactivity interrelations between the oxidation states V^{IV}, V^{III} and V^{II}. The magnetic features are of particular interest since there is a dearth of information on dinuclear vanadium complexes and it has also recently been shown that ferromagnetic coupling can occur between vanadium(III) ions in some dinuclear compounds.[13,14] It is therefore of interest to try and determine the factors which influence the nature of spin–spin coupling in d^2–d^2 systems.



H_2L

Experimental

CAUTION: Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should only be handled in small quantities.

Materials

All chemicals and solvents used were of reagent grade. Solvents used for physical measurements were of spectroscopic grade. Vanadium(III) chloride was obtained from Aldrich chemicals and stored in a nitrogen-filled desiccator and handled within a nitrogen-filled glove-bag. Aqueous $VOCl_2{\cdot}2H_2O$ (50% w/w), vanadyl sulfate trihydrate, barium chloride and barium nitrate were obtained from BDH. Barium perchlorate (Aldrich), iodide and thiocyanate were obtained from Hopkins and Williams and used as received. The preparation of the barium perchlorate salt $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ has been described previously.[2]

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† *Non-SI unit employed:* $\mu_B \approx 9.7274 \times 10^{-24}$ J T^{-1}.

Synthesis of $[V_2L(H_2O)_4]^{4+}$ complexes

The dinuclear vanadium(III) complexes of H_2L were prepared by one or more of the following routes.

***(i)* Transmetallation of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ with VCl_3.** The barium perchlorate salt of H_2L (0.6 g, 0.744 mmol) was suspended in a stirred methanol solution (50 cm^3) and slowly brought to reflux temperature. Solid VCl_3 (0.234 g, 1.48 mmol) was added to the hot solution and a deep purple colouration developed. Heating was continued for 3 h, the solution filtered and the filtrate evaporated to dryness. The resultant purple residue was redissolved in acetonitrile and filtered to remove an insoluble purple solid (**1**) and yield a wine-red filtrate which, on treatment with diethyl ether, precipitated a maroon solid (**2**). These compounds were recrystallized from methanol and dried *in vacuo*.

$[V_2L(H_2O)_4][ClO_4]_2Cl_2$ **1** (Found: C, 32.7; H, 3.7; Cl, 16.3; N, 9.7. $C_{24}H_{36}Cl_4N_6O_{14}V_2$ requires C, 32.9; H, 4.1; Cl, 16.2; N, 9.6%): IR (Nujol, cm^{-1}) 3500–3200s (br), 1638s, 1601s, 1320w, 1300w, 1269s, 1210m, 1115s (br), 1030m, 1000m, 918m, 820s, 755s, 697s, 660w, 650w and 625s.

$[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ **2** (Found: C, 28.2; H, 4.2; Cl, 13.6; N, 8.0. $C_{24}H_{38}Cl_4N_6O_{23}V_2$ requires C, 27.6; H, 3.7; Cl, 13.6; N, 8.1%): IR (Nujol, cm^{-1}) 3550–3200vs (br), 1637s, 1601s, 1320w, 1298w, 1268s, 1209m, 1108vs (br), 917m, 819m, 754m, 696s, 667w, 651w and 624s.

***(ii)* Transmetallation of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ with $VO(SO_4){\cdot}3H_2O$.** To a stirred methanolic solution (50 cm^3) containing $Ba(ClO_4)_2$ (0.209 g, 0.62 mmol) and a suspension of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (0.5 g, 0.62 mmol) was added $VO(SO_4){\cdot}3H_2O$ (0.269 g, 1.24 mmol). An immediate darkening resulted on complete dissolution of the reactants. The solution was slowly and carefully brought to reflux temperature. After 3 h it was filtered to remove an insoluble precipitate ($BaSO_4$) and retrieve an intense purple filtrate. The filtrate was taken to dryness, redissolved in acetonitrile, filtered and reprecipitated with the addition of diethyl ether. Recrystallization from acetonitrile gave a maroon microcrystalline solid, which was dried *in vacuo*. The physicochemical properties of the solid indicated that it was identical to the perchlorate complex **2** described above.

***(iii)* Template formation of $[V_2L(H_2O)_4][SO_4]_2{\cdot}H_2O$ 3 and $[V_2L(H_2O)_4]Cl_4{\cdot}5H_2O$ 4 *via* the action of (*a*) $VO(SO_4){\cdot}3H_2O$ and (*b*) $VOCl_2{\cdot}2H_2O$ upon 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol.** Equimolar quantities of either (*a*) $VO(SO_4){\cdot}3H_2O$ or (*b*) $VOCl_2{\cdot}2H_2O$ (50% aqueous solution) and 2,6-diacetylpyridine were dissolved in methanol. The stirred solution was slowly brought to reflux temperature. One mole equivalent of a methanolic solution of 1,3-diaminopropan-2-ol was added, dropwise, over ≈30 min. The initial blue-green solution lightened with the addition and a white precipitate became evident. The solution was refluxed for 16 h. The resultant deep blue-purple solution was filtered whilst hot and evaporated to dryness on a rotary evaporator. The residue was recrystallized from methanol to yield dark blue-purple microcrystals which were dried *in vacuo*.

$[V_2L(H_2O)_4][SO_4]_2{\cdot}H_2O$ **3** (Found: C, 35.3; H, 4.7; N, 10.0; S, 7.6. $C_{24}H_{38}N_6O_{15}S_2V_2$ requires C, 35.3; H, 4.7; N, 10.3; S, 7.8%): IR (Nujol, cm^{-1}) 3500–3200s (br), 1639s, 1596s, 1316w, 1270s, 1111vs (br), 1049vs (br), 984m, 917w, 820m, 752m, 721w and 686m.

$[V_2L(H_2O)_4]Cl_4{\cdot}5H_2O$ **4** (Found: C, 34.0; H, 4.9; Cl, 17.1; N, 10.0. $C_{24}H_{46}Cl_4N_6O_{11}V_2$ requires C, 34.3; H, 5.4; Cl, 16.9; N, 10.0%): IR (Nujol, cm^{-1}) 3500–3100vs (br), 1634s, 1600s, 1320w, 1270m, 1210m, 1170s, 1120s, 1000m, 920m, 816m, 750w and 695s.

***(iv)* Metathetical precipitation reactions of complex 3 with $Ba(ClO_4)_2$, $BaCl_2$, $Ba(SCN)_2$, $Ba(NO_3)_2$ and BaI_2.** A typical procedure was as follows: $[V_2L(H_2O)_4][SO_4]_2{\cdot}H_2O$ **3** was dissolved in water with vigorous stirring. A 2 mole equivalent of the barium salt was added. The solution was then stirred and heated for 0.5 h to ensure complete exchange of the anion. The resultant solution was allowed to settle and cooled in an ice-bath, decanted, filtered and centrifuged to remove the insoluble $BaSO_4$. The aqueous filtrate was evaporated to dryness and the product recrystallized from methanol. The resulting microcrystalline solids were filtered off and dried *in vacuo*. The perchlorate (**2**) and chloro (**4**) species prepared by this method were found to have identical physicochemical properties to those described above.

$[V_2L(H_2O)_4][SCN]_4$ **5** (Found: C, 40.0; H, 3.9; N, 16.5. $C_{28}H_{36}N_{10}O_6S_4V_2$ requires C, 40.1; H, 4.3; N, 16.7%): IR (Nujol, cm^{-1}) 3450s (br), 2082vs, 1631s, 1594s, 1313m, 1294w, 1266s, 1205s, 1121s, 1073w, 996w, 917m, 817s, 751m, 721w, 696s and 648w.

$[V_2L(H_2O)_4][NO_3]_4{\cdot}2H_2O$ **6** (Found: C, 32.1; H, 4.2; N, 15.7. $C_{24}H_{40}N_{10}O_{20}V_2$ requires C, 32.2; H, 4.3; N, 15.7%): IR (Nujol, cm^{-1}) 3500–3100vs (br), 1638s, 1599s, 1450–1300s (br), 1267s, 1208s, 1119s, 1073m, 1041w, 1021m, 917w, 823s, 755m, 698s and 667w.

$[V_2L(H_2O)_4]I_4{\cdot}8H_2O$ **7** (Found: C, 22.9; H, 3.8; I, 40.5; N, 6.6. $C_{24}H_{52}I_4N_6O_{14}V_2$ requires C, 22.9; H, 4.1; I, 40.4; N, 6.7%): IR (Nujol, cm^{-1}) 3200vs (br), 1635s, 1597s, 1318w, 1299w, 1267m, 1210s, 1106s, 1069s, 1021w, 998w, 983w, 915m, 821m, 778w, 752m, 721w, 696s, 645m and 608m.

Attempted chemical oxidation of complex 2

To an acetonitrile solution containing complex **2** (0.2 g, 0.192 mmol) was added, with vigorous stirring, a four-fold excess of iodosylbenzene. The solution was stirred for 10 min (longer periods were found to produce ligand oxidation). The mixture was filtered to remove unreacted iodosylbenzene and the filtrate reduced in volume and precipitation induced by the addition of diethyl ether to yield a purple solid. The solid was washed with acetone and diethyl ether to remove any iodosylbenzene and dried *in vacuo*. The infrared spectrum of this solid was identical to that of the starting material. It was found to be ESR silent (no V^{IV} present) and possessed a room-temperature magnetic moment of 2.20 μ_B per V. Similar treatment with an excess of hydrogen peroxide also proved ineffective, and resultant work-up led to the recovery of the starting vanadium(III) species.

Physical methods

Infrared spectra were measured on a Perkin-Elmer 1600 FT-IR instrument with the samples as Nujol mulls between NaCl plates (s = strong, m = medium, w = weak, sh = shoulder, br = broad). Chemical analyses (C, H, N, S, Cl, I) were performed by the Commonwealth Micro-Analytical Services, Melbourne, Australia. Ultraviolet–visible spectra were recorded on a Hitachi 150–20 spectrophotometer using 1 cm quartz cells and solution concentrations of 10^{-4} mol dm^{-3}. Magnetic moments at room temperature were determined using a Faraday balance which incorporated a Newport electromagnet fitted with Faraday-profile pole faces. The instrument was calibrated using $[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine) and $CuSO_4{\cdot}5H_2O$. Diamagnetic corrections for ligand susceptibilities were made using Pascal's constants. Variable-temperature magnetic susceptibility measurements (300–4.2 K) were performed on powdered samples at a field strength of 10 000 G (1 T) using a Quantum Design M.P.M.S. Squid magnetometer. The calibration of the instrument was checked regularly against samples of pure palladium and AR $CuSO_4{\cdot}5H_2O$. Samples were enclosed in gelatin capsules suspended at the middle of a plastic drinking straw, which was rigidly fixed to the end of the sample rod. The ESR spectra were recorded on neat powdered samples measured at 9.1 GHz using a Varian E12 instrument fitted with a liquid-nitrogen cryostat. Cyclic voltammetry measurements were carried out using a Bioanalytical System BAS-100 instrument with a three-electrode cell equipped with a platinum or glassy carbon working electrode, a platinum-wire auxiliary electrode and a saturated calomel (SCE) reference electrode. All measurements were recorded at room temperature in dry, degassed acetonitrile [$\approx$(1–2) × 10^{-3} mol dm^{-3}] with tetrabutylammonium perchlorate ($\approx$0.1 mol dm^{-3}) as the supporting electrolyte. Scan rates between 50 and 1000 mV s^{-1} were generally employed, the most common being 100 mV s^{-1}.

Results and Discussion

Synthesis and characterization

We had previously shown that complex **2**, of stoichiometry $[V_2L(H_2O)_4][ClO_4]_4\cdot2H_2O$, may be prepared by using a transmetallation technique,[9,15] in which a methanolic solution of the barium salt $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ was treated with solid VCl_3, to yield a purple product. An X-ray diffraction study upon a single crystal, grown from an aqueous solution of the compound, gave the molecular structure shown in Fig. 1. It is interesting that, in the present study, recrystallization from ethanol also yielded the water-ligated species rather than a methanolate, the source of water presumably being the original barium complex, or air. Microanalytical data marginally favour a monohydrate in the present work rather than a dihydrate as first reported.[9] The compounds are the same.

That vanadium ions in the +3 oxidation state remained incorporated within the macrocyclic cavity was somewhat surprising since the reaction conditions employed (aerobic and with no precaution to exclude water from the system) would normally be expected to result in the isolation of oxovanadium(IV) products. It was postulated that the ligand provided favourable donor atom and/or geometrical characteristics, capable of having a stabilizing influence toward vanadium(III).

In addition to extending this single example into a series of vanadium(III)–L compounds and investigating their magnetic, electrochemical and reactivity properties, a basic tenet behind the present study was to ascertain whether oxovanadium(IV) species, co-ordinated within the macrocyclic cavity, were attainable. Several preparative methods were employed in an attempt to achieve this result including: (*i*) incorporation of VO^{2+} within the performed $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ macrocycle, *via* a transmetallation technique, similar to that used previously but utilizing oxovanadium(IV) precursors in the place of VCl_3; (*ii*) direct incorporation of VO^{2+} within the macrocycle *via* the template action of oxovanadium(IV) precursors upon 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol, and (*iii*) oxidation of the vanadium(III)-containing macrocyclic compounds, $[V_2L(H_2O)_4]^{4+}$, through electrochemical or chemical means.

Thus, on dropwise addition of a methanolic solution containing vanadyl sulfate, $VO(SO_4)\cdot3H_2O$, to a refluxing methanolic solution consisting of barium perchlorate and a suspension of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (2 : 1 : 1), a discernible darkening, from light blue to deep purple, was noted after several minutes. This would tend to indicate that the reduction of V^{IV} to V^{III} was taking place almost immediately, with concomitant co-ordination to the macrocyclic ligand. The resultant product was found to exhibit properties typical of the dinuclear vanadium(III)-containing species isolated previously. The product possessed a reduced magnetic moment (μ_{eff} 2.30 μ_B per V at 295 K) and no ESR signal anticipated for a vanadium(IV) product, whether it be mono- or di-nuclear. The infrared spectrum and elemental analyses further identified this product as being $[V_2L(H_2O)_4][ClO_4]_4\cdot H_2O$ **2**.

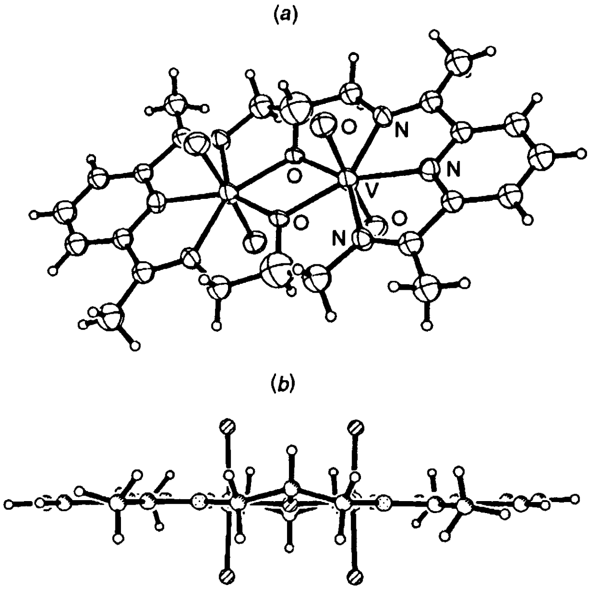
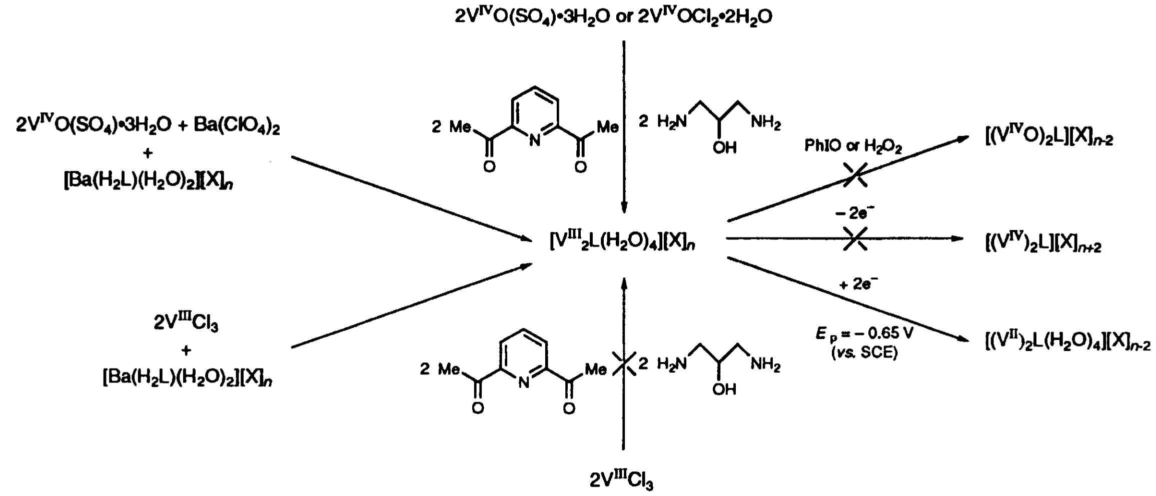


Fig. 1 (*a*) Molecular structure of the cation $[V_2L(H_2O)_4]^{4+}$; (*b*) Side-on perspective (see ref. 9 for crystallographic details)

Incorporation of two vanadium(III) ions within the macrocyclic cavity also resulted from the template action of oxovanadium(IV) salts, such as $VO(SO_4)\cdot3H_2O$ or $VOCl_2\cdot2H_2O$, upon 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol. No evidence was obtained for any vanadium(IV)-containing species having been produced en route. Formation of the macrocyclic complex was evident by the disappearance of carbonyl (1705 cm^{-1}) and amine (3100–3200 cm^{-1}) stretching frequencies in the infrared spectrum, and the appearance of a characteristic new band, assignable to the imine moiety, at 1630–1640 cm^{-1}. Except for differing anion peaks, these infrared spectra are identical to those of compounds formed previously using vanadium(III) trichloride. The absence of any vanadyl-containing species was also apparent within the infrared spectra of these compounds, as there were no new bands in the 800–1000 cm^{-1} region, which would be expected to result from the vanadyl (V=O) stretching frequency. The reaction is not hindered in any way by the presence of water as laboratory-grade solvents and aquated vanadium salts were utilized ($VOCl_2\cdot2H_2O$ as a 50% aqueous solution). Further, the reduction of V^{IV} to V^{III} occurred under aerobic conditions, with no precautions made to exclude oxygen from the system. Such conditions would normally be expected to yield oxovanadium(IV) or even vanadium(V) products.

The possible use of V^{III} as a templating ion in the formation of the macrocycle was also investigated. This was not successful. Isolated products were found to exhibit a band at 1695 cm^{-1} in the infrared spectrum, indicative of a carbonyl-containing species, which suggests the product was a complex of an incompletely closed macrocycle. This behaviour has been noted previously by Fenton and co-workers,[2] for strontium-containing complexes of the macrocycle, and by Dutton[15] during preliminary work on vanadium compounds of L.

Vanadium(IV) species thus undergo reduction, either mediated by the already formed macrocycle, or by the reaction media. They will thus act as template ions, with concomitant reduction to V^{III} during formation of the macrocycle, or themselves be reduced and incorporated within the preformed macrocycle. Whereas VCl_3 will be incorporated into the preformed macrocycle, without subsequent oxidation, it does not act as an efficient templating ion (Scheme 1). The *in situ* reduction of V^{IV} to V^{III} and simultaneous loss of the oxo group is not without precedent in vanadium chemistry. Nakanishi and co-workers[16] reported that partial substitution and reduction of $[VO(acac)_2]$ (acac = pentane-2,4-dionate) by the triphenol, pyrogallol, occurred to yield a pyrogallol-bridged vanadium(III)



Scheme 1

dimer complex, $[V_2(acac)_4\{\mu\text{-}OC_6H_3(OH)_2\}_2]$. It is also believed that the large amounts of tunichrome present in the blood of *Ascidia nigra* may participate in the reduction of V^V to V^{III} *in vivo.*[17]

There not only appears to be a stabilizing influence towards having V^{III} co-ordinated within the macrocyclic cavity, as mentioned above, but a driving force to exclude the incorporation of V^{IV}. Attempts to form dinuclear vanadium(III) or -(IV) complexes of the macrocyclic ligand containing the longer pentan-3-ol backbone, formed *via* the reaction of $VO(SO_4)\cdot 3H_2O$, 2,6-diacetylpyridine and 1,5-diaminopentan-3-ol, proved ineffective as the $VO(SO_4)\cdot 3H_2O$ failed to act as a template in the formation of the macrocycle. This macrocycle has previously been formed through the action of barium as the templating ion,[2] and it has an identical donor-atom set to that of the present macrocycle. The failure to identify any macrocyclic species within the isolated products lends weight to the assertion that it is more likely a combination of donor atom and favourable geometrical characteristics of H_2L that gives rise to the surprising stability of the vanadium(III) complexes, than purely favourable donor-atom properties.

As previously noted,[15] treatment of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ with VCl_3 not only led to the formation of $[V_2L(H_2O)_4][ClO_4]_4\cdot H_2O$, but also to the isolation of a series of compounds of varying chloroperchlorate stoichiometry. This behaviour was again noted in the present study. It was difficult to obtain stringent control over the formation of these Cl^-/ClO_4^- compounds, and so products were obtained in lower than expected yield and of uncertain composition. In order to obtain larger yields and to control the anion content more judiciously a more amenable procedure was sought. A method of achieving this end was realized by taking advantage of the relatively high-yielding and anion-selective preparation of the sulfate-containing compound $[V_2L(H_2O)_4][SO_4]_2\cdot H_2O$ **3**, prepared *via* route (*ii*) above. Thus, careful anion metathesis, through the treatment of aqueous solutions of **3** with various barium salts, followed by subsequent removal of the insoluble $BaSO_4$, yielded a series of dinuclear vanadium(III) compounds of composition $[V_2L(H_2O)_4][X]_4\cdot nH_2O$ (X = ClO_4, Cl, SCN, I or NO_3; n = 0–8). These compounds displayed the characteristics specific to the vanadium(III) complexes previously identified and are assumed, from their similar infrared, UV/VIS spectra and magnetic properties (Table 1), to all possess the same cation as that structurally characterized in the perchlorate complex $[V_2L(H_2O)_4][ClO_4]_4\cdot 2H_2O$.

Magnetic exchange in $[V_2L(H_2O)_4]^{4+}$ complexes

The observed magnetic moments at 295 K for the dinuclear vanadium(III) compounds are presented in Table 1. It is evident that the effective magnetic moments of the complexes are reduced from the spin-only value expected for non-coupled dinuclear vanadium(III) systems, 2.83 μ_B per vanadium. This would indicate that an antiferromagnetic interaction is operating between the vanadium(III) centres. The magnitude of the exchange interaction between metal centres is commonly evaluated by a study of the magnetic susceptibility as a function of temperature. Thus, magnetic susceptibilities were measured in the temperature range 4.2–300 K for neat powdered samples of $[V_2L(H_2O)_4][ClO_4]_2Cl_2$ **1** and $[V_2L(H_2O)_4][SCN]_4$ **5**. Plots of molecular susceptibility and magnetic moment *vs.* temperature for **1** are shown in Fig. 2. Those for **5** are very similar.

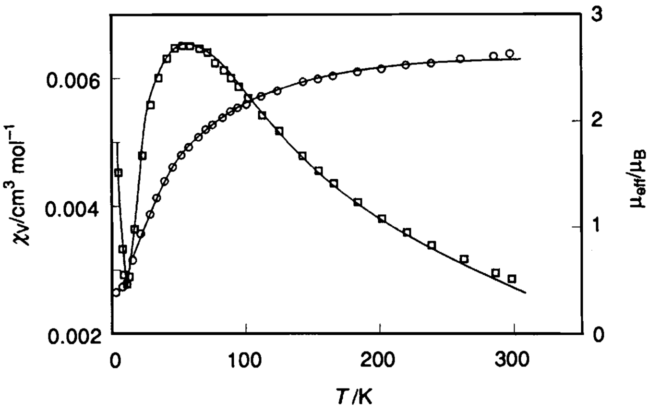


Fig. 2 Temperature dependence of the magnetic susceptibility (□) and magnetic moment (○) for $[V_2L(H_2O)_4][ClO_4]_2Cl_2$ **1**. The solid line is that calculated using the parameters in Table 2

The molecular susceptibility plots exhibit the characteristic appearance of antiferromagnetically coupled systems. In the case of complex **1** there is a maximum centred at *ca.* 55 K followed by a minimum at *ca.* 12 K and a Curie tail below 12 K. The thiocyanate complex **5** displays similar behaviour with a maximum centred at *ca.* 65 K followed by a minimum at *ca.* 15 K. The corresponding magnetic moments, per vanadium, decrease from 2.85 to 0.4 μ_B for **1** and from 2.70 to 0.40 μ_B for **5**. Such behaviour is indicative of an antiferromagnetically coupled system combined with the presence of a small amount of paramagnetic impurity. The experimental data for **1** and **5** closely follow a modified Bleaney–Bowers[18] equation for an $S = 1$ dimer appropriate to dinuclear vanadium(III) complexes (Table 2). This simple $-2JS_1\cdot S_2$ approach is strictly applicable to orbitally non-degenerate (A) ground-state ions. Presumably any orbital degeneracy in the present system is tempered by the low-symmetry ligand field. After corrections were made for a θ

Table 1 Magnetic moments (μ_B), selected infrared and electronic absorption peaks for the $[V_2L(H_2O)_4][X]_y{\cdot}nH_2O$ complexes (y = 2 or 4; n = 0–8)

Compound	μ_{eff} (295 K)[a]	Infrared absorption peaks (cm^{-1}) v(C=N)	v(C=C)	v(anion)	Electronic absorption peaks[b]
1 $[V_2L(H_2O)_4][ClO_4]_2Cl_2$	2.85	1638	1601	1115 (br), 625	292 (8353), 302 (8975), 313 (sh) (7762), 470 (1555), 528 (1613)
2 $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$	2.26	1637	1601	1108 (br), 624	291 (8781), 302 (9057), 314 (sh) (7455), 472 (1364), 520 (1403)
3 $[V_2L(H_2O)_4][SO_4]_2{\cdot}H_2O$	2.70	1639	1596	1111 (br)	291 (8148), 302 (8223), 314 (sh) (6785), 470 (1320), 535 (1364)
4 $[V_2L(H_2O)_4]Cl_4{\cdot}5H_2O$	2.41	1634	1600	—	295 (8603), 302 (9687), 313 (sh) (7993), 470 (1645), 532 (1974)
5 $[V_2L(H_2O)_4][SCN]_4$	2.70	1631	1594	2082	*c*
6 $[V_2L(H_2O)_4][NO_3]_4{\cdot}2H_2O$	2.58	1638	1599	1450–1300 (br)	293 (8826), 302 (9067), 314 (sh) (7321), 470 (1633), 532 (1685)
7 $[V_2L(H_2O)_4]I_4{\cdot}8H_2O$	2.60	1635	1597	—	292 (8505), 302 (8952), 313 (sh) (7532), 470 (1697), 532 (1426)

[a] μ_B per V. [b] In water; λ/nm (ε/dm^{-3} mol^{-1} cm^{-1} per dimer), sh = shoulder. [c] Only slightly soluble in water.

Table 2 Parameters used to fit the susceptibility data to a modified Bleaney–Bowers[18] equation for $S_1 = S_2 = 1$

Compound	g	J/cm^{-1}	θ/cm^{-1}	Monomer (%)
1	1.94	−20	−2.0	2.9
5	2.04	−25	−3.7	3.7
	(±0.01)		(±1.0)	(±0.02)

(intermolecular) coupling term (*i.e.* $T - \theta$) and for the presence of a monomeric impurity, the data were satisfactorily described by this model. The g value for the paramagnetic impurity was assumed to take the same value as that of the complex.

Magnetic susceptibility studies conducted upon two structurally related alkoxo-bridged dinuclear vanadium(III) complexes,[19,20] $[V_2L^1{}_2]^{2-}$ and $[V(HL^2)_2]^{2-}$, where L^1 = $(^-O_2CCH_2)_2NCH_2CH(O^-)CH_2N(CH_2CO_2{}^-)_2$ and L^2 = $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CH_2OH)(CH_2CO_2{}^-)$, in which bonding to the metal centres is similarly disposed in a pentagonal-bipyramidal array, led to values for the coupling parameter, J, of −14.5 and −8.5 cm^{-1} respectively (Table 3). Thus, it may be seen that the antiferromagnetic interaction occurring within the present compounds, though slightly stronger, is of a comparable magnitude to those experienced within the $[V_2L^1{}_2]^{2-}$ and $[V(HL^2)_2]^{2-}$ complexes and it is weak in all cases.

Magnetic susceptibility studies upon other dinuclear vanadium(III) complexes, where bridging is furnished by oxygen-donor groups, include the pyrogallol-bridged compound $[V_2(acac)_4\{\mu\text{-}OC_6H_3(OH)_2\}_2]$[16] ($J$ = −22.4 cm^{-1}), the μ-oxo-di-μ-acetato (J = +18 to > +200 cm^{-1}) and the μ-hydroxy-di-μ-acetato (J = −36 cm^{-1}) complexes incorporating 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn),[13,14] and a μ-oxo 2,2′-bipyridyl complex, $[\{VCl(bipy)_2\}_2O]Cl_2$ (J positive).[21] These compounds possess a range of different geometrical co-ordination around the metal centres, which gives rise to the varied magnetic behaviour. The interactions are predominantly antiferromagnetic in nature. It appears that μ-oxo V^{III}–O–V^{III} bridges lead to nett positive J values, whilst V–O(X)–V bridges (X = H, aryl or alkyl) lead to nett antiferromagnetism (negative J values). Knopp and Wieghardt[14] explained the sign change in the tmtacn pair in terms of a super-exchange model in which the z direction is taken as being along the short (bridging) V–O axis. Ferromagnetism arises from the 'crossed pathway' $d_{z^2}{}^0|O_p|d_{xz}{}^1$ interaction dominating the antiferromagnetic $d_{yz}{}^1|O_p|d_{yz}{}^1$ pathway. Removal of electron density from the O^{2-} bridge on protonation weakens the V–O bond and reduces the orbital overlap between the metal centres (*via* the oxygen-bridge). The effect is most dramatic upon the ferromagnetic term and serves to remove this pathway from the superexchange mechanism, resulting in the predominance of the antiferromagnetic term.

The bridging alkoxo group in the backbone of the molecular structure of H_2L adopts a trigonal disposition and so is ideally set up to communicate an interaction between metal centres, through a superexchange mechanism. Other known dinuclear complexes of H_2L include the copper(II) and iron(III) species investigated by McKee and co-workers.[6,7] An acetonitrile solution of the complex $[Cu_2(HL)(MeCN)(H_2O)][ClO_4]_3$, in which bridging is through only one alkoxo group, with the other remaining protonated, gave no ESR spectrum at room temperature or as a frozen solid at 4 K. This suggested considerable spin exchange was occurring between the copper centres, a situation confirmed by a variable-temperature susceptibility study which yielded a singlet–triplet, 2J, energy separation of −84 cm^{-1}. The magnitude of the magnetic exchange integral, J, for the $[Fe_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ complex was found to be −11.1 cm^{-1}.

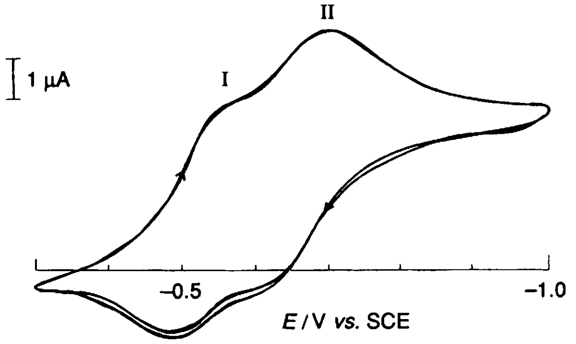


Fig. 3 Multiple-sweep cyclic voltammogram for an acetonitrile solution of $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ **2** at a platinum electrode. Scan rate 100 mV s^{-1} (SCE reference electrode)

Electrochemistry of $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ 2 in acetonitrile solution

The cyclic voltammetry (CV) behaviour of complex **2**, determined at a platinum-button electrode in an ≈1 × 10^{-3} mol dm^{-3} acetonitrile solution, is displayed in Fig. 3. It is evident that there are two reduction waves occurring at the platinum electrode under the conditions employed. These are ascribed to processes labelled I and II. Similar behaviour is also observed at a glassy carbon electrode. Process I is separated from II by some 120–130 mV. The close proximity of the processes to each other makes difficult the determination of individual peak currents. Nevertheless, the peak currents appear to remain constant with changing scan rate, and in a qualitative sense with respect to the reductive and oxidative events occurring at each process, **2** exhibits quasi-reversible behaviour since the peak differences $E_p{}^f - E_p{}^r$ show some slight dependence upon scan rate. Process I occurs at a half-wave potential of −0.53 V (relative to the SCE and scan rate of 100 mV s^{-1}) and II at −0.65 V under the same conditions. These half-wave potentials were found to be essentially independent of scan rate. The cathodic-to-anodic peak separations for process I and II are in the order of 70–85 mV. The cyclic voltammetry of $[Ba(H_2L)(H_2O)_2][ClO_4]_2$, under identical

Table 3 Magnetostructural data for alkoxo-bridged dinuclear vanadium(III) complexes with pentagonal-bipyramidal co-ordination

Compound	V–O–V/°	O–V–O/°	V···V/Å	*g*	*J*/cm^{-1}
$[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ **2**	111.4	68.6	3.276	1.87	−25
$K_2[V_2L^1{}_2]{\cdot}7H_2O$ [19]	110.3	69.7	3.343	1.88	−14.5
$[H_2en][V(HL^2)_2]_2{\cdot}2H_2O$ [20,*]	108	72	3.296	1.93	−8.5

* en = Ethane-1,2-diamine.

$$V^{III}\text{–}V^{III} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} V^{II}\text{–}V^{III} \underset{-e}{\overset{+e}{\rightleftharpoons}} V^{II}\text{–}V^{II}$$

Process I −0.53 V

Process II −0.65 V

Scheme 2 Electrochemical processes occurring at a platinum electrode for the complex $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ **2** (scan rate 100 mV s^{-1})

conditions, showed no evidence of any electrochemical activity at these potentials (+0.50 to −1.40 V), and so the electrochemical behaviour observed for the vanadium(III) dinuclear complex would appear to be metal centred.

These observations may be ascribed to the two sequential one-electron transfers shown in Scheme 2. The separation between processes I and II, of 120–130 mV, compares with the corresponding separation of 260 mV for the related processes within the μ-oxo-di-μ-benzoato vanadium(III) tmtacn (L) complex $[V_2L_2(\mu\text{-}O)(\mu\text{-}O_2CPh)_2]I_2{\cdot}H_2O$.[13] The position of and separation between the processes in the latter complexes were also found to be highly dependent upon the character of the bridging carboxylate. The doubly reduced forms of these complexes, $V^{II}{}_2$, were very unstable in solution and only evident at very negative potentials (−2.1 V *vs.* ferrocenium–ferrocene). The comparative ease at which the doubly reduced form is attained within the present study (−0.65 V *vs.* SCE, −1.19 V *vs.* ferrocenium–ferrocene) again shows the preference for and the stability of lower-oxidation-state vanadium ions bound by H_2L. There was no evidence for there being any oxidation of the vanadium(III) centres to any vanadium(IV)-containing species within the potential limits imposed by the present solvent conditions (−1.50 to +1.50 V, *vs.* SCE).

Chemical reactivity of $[V_2L(H_2O)_4][ClO_4]_4{\cdot}H_2O$ 2

With the aim of incorporating V^{IV} within the ligand environment, an attempt was made to oxidize complex **2** by use of chemical oxidants. Thus, an acetonitrile solution containing the compound was treated with an excess of the oxygen-transfer agent iodosylbenzene. The product isolated was found to exhibit the characteristic properties of the starting material and hence no oxygen-atom transfer or subsequent oxidation had occurred. Prolonged exposure to iodosylbenzene led to ligand oxidation. A carbonyl stretching frequency (*ca.* 1695 cm^{-1}) became apparent in the infrared spectrum of the product. Treatment of a solution containing $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ verified this assignment, as a carbonyl stretching frequency (*ca.* 1700 cm^{-1}) also occurred in the infrared spectrum of the isolated product. Treatment of an aqueous solution of the compound with an excess of hydrogen peroxide also failed to produce any oxidized species, resulting only in recovery of the starting material.

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