Preparation and some Properties of Vanadium(III) Tris(metaphosphate) and Vanadium(IV) Bis(metaphosphate)

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Vanadium(IV) bis(metaphosphate), $[VO][PO_3]_2$ (d^1), and vanadium(III) tris(metaphosphate), $V[PO_3]_3$ (d^2), have been prepared by heating V_2O_5 in phosphoric acid. Blue crystals of $[VO][PO_3]_2$ are tetragonal, space group $I4_1md$, with lattice parameters a_0 = 10.973(10), c_0 = 4.293(4) Å, and Z = 4. Green crystals of $V[PO_3]_3$ are monoclinic, space group Cc, with lattice parameters a_0 = 13.19(1), b_0 = 19.08(2), c_0 = 9.42(1) Å, β = 127° 08(6)′, and Z = 12. The bis(phosphate) probably contains chains of corner-shared $[VO_6]^{8-}$ octahedra linked by metaphosphate ($([PO_3]^-)_\infty$) chains. The tris(phosphate) is structurally similar to the C-type metaphosphates of Mo, Ti, Cr, Fe, and Al. Both compounds are resistant to most solvents and stable in air to at least 1 000 °C and have been characterised by magnetic-susceptibility and electronic-spectral measurements. Neither compound shows magnetic ordering down to 1.5 K. Possible non-linear optical properties of $[VO][PO_3]_2$ are mentioned.

ALTHOUGH many studies of condensed phosphate systems have been made,[1] the structure and properties of a number of transition-metal phosphate systems have not been well established. In fact, since the recent preparation [2,3] of the rare-earth pentaphosphates and the discovery [4,5] of the unusual fluorescence properties of Nd^{3+} in $Nd[P_5O_{14}]$, these compounds have quickly become more thoroughly characterised [6-8] than some $3d$ transition-metal phosphates. Several investigations of bivalent metal phosphates of empirical formula $M^{II}[P_2O_6]$ have been reported,[1,9,10] the structure of the cubic tetrametaphosphates of trivalent Ti, Fe, Cr, and Al is known,[11,12] and the pyrophosphates of some quadrivalent transition metals have been studied.[13,14] Structural data do not appear to be complete, however, for these latter compounds,[13,14] or for the triphosphates of titanium, aluminium, iron, and chromium.[12,15-18]

Clearly lacking is knowledge of the phosphates of reduced vanadium. Only the quadrivalent vanadium compound $[VO][PO_3]_2$ has been mentioned.[19] It was prepared [19] by dehydration of $VO_2{\cdot}P_2O_5{\cdot}2OH_2$ formed from a solution of VO_2 in phosphoric acid at 180 °C. The turquoise blue colour, the extreme insolubility in most solvents, and the frequencies of some i.r. lines of $[VO][PO_3]_2$ were the only properties listed.[19] This lack

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of attention is perhaps surprising as, apart from any chemical interest, such materials might be expected to be useful starting reagents for the preparation of controlled-valency vanadium phosphate glasses.[20,21] The reduction of V^V to V^{IV} and V^{III} in concentrated H_2SO_4 with the evolution of oxygen, and in concentrated HCl, HBr, and HI with evolution of the corresponding halogen, has long been well known.[22,23] Surprisingly, however, no report of the reducing action of concentrated phosphoric acid towards the higher oxidation states of vanadium, nor of the compounds thus formed, has been made.

In this paper we report the preparation of $[VO][PO_3]_2$ and $V[PO_3]_3$ by reduction of quinquevalent vanadium in hot H_3PO_4. This is the first preparation of $V[PO_3]_3$. Crystallographic, magnetic, optical, and spectral properties are given.

RESULTS

Preparative Conditions and Crystal Properties.—Both compounds were prepared by heating a solution of V_2O_5 in phosphoric acid (both Fisher ' certified ' reagents). Typical concentrations were 5—10 g V_2O_5 per 100 cm^3 85% H_3PO_4. No significant reduction occurred on heating to *ca.* 300 °C and a water-soluble V^V phosphate hydrate ($[VO][PO_4]\cdot xOH_2$, $x =$ *ca.* 2) may be extracted. This material is well known and thermal gravimetric and differential thermal analyses (t.g.a. and d.t.a.) showed reasonable agreement with the dehydration and melting temperatures previously observed.[24-26] The crystal structures of anhydrous α- and β-$[VO][PO_4]$ have recently been established,[27,28] showing them to be structurally similar to α- and β-$[VO][SO_4]$ respectively.[29,30]

On further heating to 350—400 °C, however, reduction to V^{IV} occurred with evolution of oxygen. The reduction under standard conditions (298 K) may be described by equation (1). As is the case in H_2SO_4, the high acidity

$$4[VO_2]^+ + 4H^+ \longrightarrow 4[VO]^{2+} + 2H_2O(l) + O_2(g) \quad (1)$$
$$E^{\ominus} = -0.23\ V$$

and loss of water vapour and oxygen from the solution under the conditions used help to overcome the unfavourable free energy under standard conditions. The solution changed from dark red to dark blue-green and anhydrous crystals of blue $[VO][PO_3]_2$ were precipitated. They were extracted after pouring the hot solution into water (with care).

When the solution was further heated to $\geqslant$450 °C $[VO][PO_3]_2$ was not obtained but the vanadium was further reduced to V^{3+}. Under standard conditions this reduction is described by equation (2) and similar comments apply as for (1). Green anhydrous crystals of $V[PO_3]_3$ were precipitated. Reduction to V^{III} is observed

$$4[VO]^{2+} + 4H^+ \longrightarrow 4V^{3+} + 2H_2O(l) + O_2(g) \quad (2)$$
$$E^{\ominus} = -0.8\ V$$

in H_2SO_4 only in the presence of other cations such as $[NH_4]^+$ when ternary salts such as $[NH_4]V[SO_4]_2$ may be obtained.[22] Further reduction to V^{2+} was not observed in either situation nor was reduction of Ti^{4+} to Ti^{3+} found.

The reactions are preferably carried out in vitreous-graphite crucibles. Gold crucibles may also be used but small amounts of colloidal gold contaminate samples prepared at the higher temperatures.[31] Heating may be effected in air in a furnace or, more simply, over a gas burner.

Both $[VO][PO_3]_2$ and $V[PO_3]_3$ are insoluble in almost all conventional solvents except fused alkalis. T.g.a. up to 1 000 °C in air showed no evidence of oxidation or decomposition and the crystals were recovered unchanged on cooling. These are unusual properties for reduced vanadium compounds. Vanadium(IV) bis(metaphosphate) crystallises in small (typically 100 μm—1 mm) highly strained rods. A crystal suitable for space-group determination was found and precession photographs (Mo-K_α radiation) indicated one of the two tetragonal space groups $I4_1md$ (point group $4mm$) or $I\bar{4}2d$ (point group $\bar{4}2m$). Suitable crystals were not available to allow the point groups to be distinguished by pyroelectric,[32] piezoelectric,[32] or optical second-harmonic generation (s.h.g.) tests.[33] However, consideration of the cell dimensions and the possible atom positions indicated $I4_1md$ to be the most likely space group (see Discussion section). Polycrystalline $[VO][PO_3]_2$ generated 0.53 μm second-harmonic radiation (*ca.* 10 times greater than the signal from polycrystalline quartz) under irradiation with 1.06 μm light from a Nd–YAG laser, in agreement with the *X*-ray evidence for an acentric space group.[33] The unit-cell dimensions are $a_0 = 10.973(10)$ and $c_0 = 4.293(4)$ Å, and the crystallographic *c* axis is parallel to the rod axis. The measured density (3.0 ± 0.1 g cm^{-3}) indicates four molecules per unit cell.

Crystals of $[VO][PO_3]_2$ are dichroic under incident polarised white light, appearing almost colourless and blue with the *c* axis parallel and perpendicular to the incident polarisation respectively. In accordance with the polarised-absorption spectra [34,35] of $[VO][SO_4]\cdot 5OH_2$ the dichroism suggests that short V–O bonds are aligned parallel to the *c* axis of the crystal. Vanadium(IV) bis(metaphosphate) is thus quite different to other quadrivalent metal diphosphates of empirical formula $M[P_2O_7]$ (M = Ge, Sn, Pb, Ti, Zr, Hf, Ce, or U) which are cubic [13,14] and contain pyrophosphate, $[P_2O_7]^{4-}$, anions. The evidence indicates that $[VO][PO_3]_2$ is very likely a linear-chain metaphosphate, with the oxygen atom closest to the vanadium not being part of the anion framework.

Vanadium(III) tris(metaphosphate) crystallises in larger

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(0.5—2 mm) more perfect rods or plates. Precession photographs (Mo-K_α radiation) indicated one of the monoclinic space groups $C2/c$ or Cc. Observation of 0.53 μm s.h.g. (*ca.* one fifth the signal from polycrystalline quartz) indicated [33] the acentric group Cc to be the correct assignment. The unit-cell dimensions are $a_0 = 13.19(1)$, $b_0 = 19.08(2)$, $c_0 = 9.42(1)$ Å, and $\beta = 127° 08(6)'$. The measured density (3.0 ± 0.1 g cm^{-3}) indicates 12 molecules per unit cell. No pleochroic effects were observed under the polarising microscope.

Analyses for total vanadium and total phosphorus were made by Schwarzkopf Microanalytical Laboratory, Woodside, New York (Found: P, 27.65; V, 22.05. Calc. for $[VO][PO_3]_2$: P, 27.55; V, 22.65. Found: P, 31.9; V, 17.9. Calc. for $V[PO_3]_3$: P, 32.3; V, 17.7%).

Spectra and Magnetic Properties.—The unusual thermal and chemical properties of $[VO][PO_3]_2$ and $V[PO_3]_3$ precluded characterisation of the vanadium species by chemical analysis for the oxidation state. Both the magnetic susceptibilities and electronic spectra, however, confirmed the presence of V^{IV} (d^1) and V^{III} (d^2) respectively.

The magnetic susceptibilities were measured from 1.5 K to room temperature using a pendulum magnetometer. The curves of magnetisation, M_g, and inverse magnetic susceptibility, $1/\chi_g$, are given in Figure 1. No evidence for magnetic ordering was found in either case, indicating magnetically isolated vanadium ions in both structures. Iron(III) tris(metaphosphate) orders antiferromagnetically at 9.5 ± 0.4 K [36] which reflects the greater exchange between d^5 Fe^{3+} than d^2 V^{3+} ions. For $[VO][PO_3]_2$ the inverse susceptibility was linear with temperature and passed through the origin [Figure 1(*a*)]. The gradient indicates a magnetic moment per V^{IV} ion of 1.67 B.M.,* close to the spin-only value for a d^1 ion of 1.73 B.M. and within the range observed for several vanadyl ($[VO]^{2+}$) compounds.[37] The plot of inverse susceptibility with temperature was slightly curved for $V[PO_3]_3$ [Figure 1(*b*)]. No attempt was made to fit the data to crystal-field parameters, but the magnetic moment derived from the highest temperature point was 2.68 B.M. per V^{3+}, slightly lower than for a spin-only d^2 ion (2.83 B.M.) and within the range commonly observed for V^{3+} salts.[38]

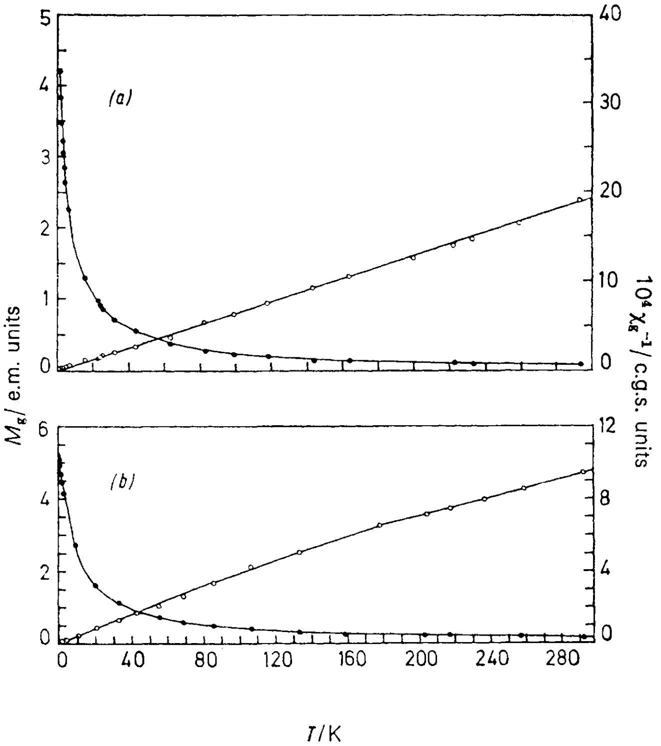

FIGURE 1 Magnetisation (●) and inverse magnetic susceptibility (○) of polycrystalline $[VO][PO_3]_2$ (*a*) and $V[PO_3]_3$ (*b*) as a function of temperature at H = 15 300 Oe

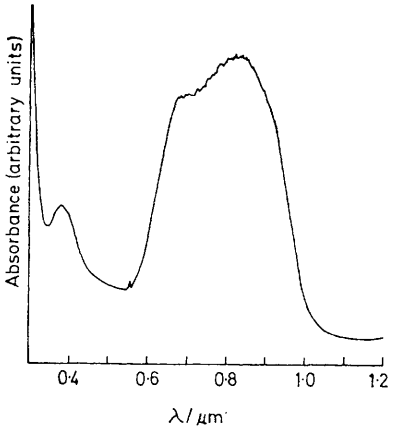

FIGURE 2 Diffuse-transmission spectrum of polycrystalline $[VO][PO_3]_2$ between 0.3 (33 333) and 1.2 μm (8 333 cm^{-1}) showing three electronic transitions at 12 050, 14 400, and 26 300 cm^{-1}

The electronic spectra were measured at room temperature by diffuse transmission through polycrystalline samples supported in a Nujol matrix. Three broad bands are observed for $[VO][PO_3]_2$ (Figure 2), centred at 12 050, 14 400, and 26 300 cm^{-1}. These are characteristic of many $[VO]^{2+}$ compounds [37] and may be assigned respectively to transitions from the $^2B_2$ ground state to ^2E, $^2B_1$, and $^2A_1$ expected for a tetragonally distorted $[VO_6]^{8-}$ octahedron,[34,35] where the V^{IV} ion is displaced towards one oxygen atom creating a long and a short V–O bond. In a molecular-orbital (m.o.) picture the levels correspond to equatorial π- ($^2B_2$), axial π- (^2E), equatorial σ- ($^2B_1$), and axial σ-bonding ($^2A_1$) states. Although the energies of the $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$ bands seem lower than often observed,[37] it is probably not profitable to discuss this in terms of bonding effects in the absence of accurate polarised single-crystal spectra.

Three bands (centred at 14 100, 22 600, and 29 400 cm^{-1}) were also observed for $V[PO_3]_3$ (Figure 3). These correspond to the three spin-allowed transitions for an octahedral d^2 ion: $^3T_{1g} \rightarrow {}^3T_{2g}$, $^3T_{1g} \rightarrow {}^3T_{1g}$, and $^3T_{1g} \rightarrow {}^3A_{2g}$ respectively.[39] The highest-energy band is obscured by charge-transfer bands in most V^{3+} compounds.[40] Using the simple crystal-field treatment outlined by Clark,[40] the

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* 1 B.M. ≈ 9.27×10^{-24} A m^2.

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ligand-field splitting parameter *Dq* and the Racah parameter *B*, together with the energy of the highest-energy band, may be calculated from the energies of the two lower-energy bands. For $V[PO_3]_3$ we find $({}^3T_{1g}\rightarrow{}^3A_{2g})_{\text{calc.}}$ at 29 460 cm^{-1}, which is probably fortuitously close to the observed energy (29 400 cm^{-1}); *Dq* and 15*B* are 1 536 and 9 750 cm^{-1} respectively, close to values observed for other octahedral oxide and fluoride compounds of V^{3+}.[40]

I.r. spectra were measured from 5 to 15 μm (2 000 to 666 cm^{-1}) in a KBr pellet. A band at 937 cm^{-1} observed for $[VO][PO_3]_2$ is assigned to V–O stretching.[37] Other bands at 675 and 820 and at 970 cm^{-1} are characteristic of symmetric and antisymmetric P–O–P stretching respectively,[41] and bands at 1 080—1 160 and 1 200—1 350 cm^{-1} are characteristic of PO_2 symmetric and antisymmetric stretching. Bands at 675—770, 970—1 050, 1 080—1 160, and 1 220—1 320 cm^{-1} for $V[PO_3]_3$ are assigned similarly.

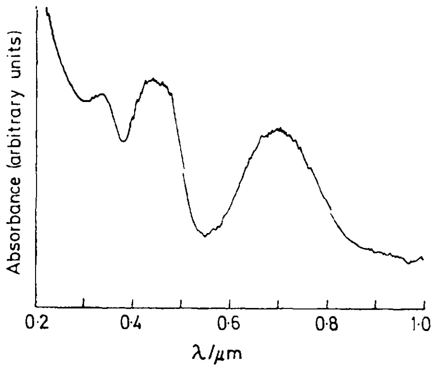

FIGURE 3 Diffuse-transmission spectrum of polycrystalline $V[PO_3]_3$ between 0.2 (50 000) and 1.0 μm (10 000 cm^{-1}) showing three electronic transitions at 14 100, 22 600, and 29 400 cm^{-1}

DISCUSSION

Hot concentrated phosphoric acid has been shown to act as a reducing agent towards V^{IV} and V^{V} oxo-compounds as was expected from the previously reported behaviour of other strong acids. Crystals of $[VO][PO_3]_2$ and $V[PO_3]_3$ were prepared by reduction of V_2O_5 dissolved in H_3PO_4. The former phosphate has been reported only once before and the latter is reported here for the first time. Both compounds possess unusual thermal stability and resistance towards solvents. The species were characterised by their magnetic behaviour and electronic spectra. As is found in most quadrivalent vanadium compounds, the V^{IV} ion in $[VO][PO_3]_2$ appears to be surrounded by an octahedron of oxygen atoms, but displaced towards one oxygen with the formation of one long and one short V–O bond. The properties of $V[PO_3]_3$ are characteristic of octahedrally co-ordinated V^{3+}.

The crystal structures have not been determined in this work. Certain deductions concerning the structure of $[VO][PO_3]_2$ may, however, be drawn from the space-group determination and the cell dimensions. The optical properties under polarised light (see above) show the short V–O bonds of the $[VO_6]^{8-}$ octahedra to be aligned parallel to the crystallographic *c* axis. The *c*-axis dimension of 4.293 Å is very close to that of $[VO][MoO_4]$ (4.2646 Å)[42] and α-$[VO][SO_4]$ (4.101 Å)[29] where chains of corner-shared $[VO_6]^{8-}$ octahedra run parallel to the *c* axis, and it is very likely that this arrangement also occurs in $[VO][PO_3]_2$. A similar arrangement is found[43] in $[VO][SiP_2O_8]$ where the repeat distance is 4.078 Å. The length of the *c* axis in $[VO][PO_3]_2$ is the sum of the long and short V–O distances and the four vanadium atoms and nearest-neighbour oxygen atoms per unit cell must lie on similar special positions of the form $(00z)$. This information indicates $I4_1md$ rather than $I\bar{4}2d$ to be the correct space group.[44] The chains of octahedra are probably linked by metaphosphate $([PO_3]^-)_\infty$ chains with the eight phosphorus atoms per unit cell at $(0yz)$ special positions, and the four equatorial oxygen atoms of each $[VO_6]^{8-}$ octahedron each being part of a different $([PO_3]^-)_\infty$ chain.

The absence of magnetic ordering in $[VO][PO_3]_2$ may be contrasted with the ferromagnetic ordering observed below 4 K in α-$[VO][SO_4]$, the antiferromagnetic ordering below 25 K in β-$[VO][SO_4]$[29] (in β-$[VO][SO_4]$ corner-sharing $[VO_6]^{8-}$ octahedra form zig-zag chains[30]), and the antiferromagnetic ordering below 2.5 K in $[VO][SiP_2O_8]$.[45] Presumably the magnetic exchange is quite sensitive to the intermediate groups and the exact crystal geometry.

Vanadium(III) tris(metaphosphate) is apparently isomorphous with the *C*-type monoclinic metaphosphates of Al^{3+} and Fe^{3+},[17] Cr^{3+},[18] Ti^{3+},[12] and Mo^{3+}.[46] The space groups of the latter two compounds were given as body-centred monoclinic *I*2/*a* or *Ia*, which is simply transformed to the true *C*-centred cell. Although several polymorphs of the Al, Fe, and Cr metaphosphates are known,[17,18] the monoclinic phase is the thermally stable form for all except Al where the cubic tetrametaphosphate is the final product of heating.[17] No evidence was obtained in this work for polymorphs of $V[PO_3]_3$. None of these structures seems to have been determined except for the tetrametaphosphate,[11] but the monoclinic form is stable over a fairly wide range of cationic radii [Ti^{3+} and Mo^{3+} (0.67 Å) down to Al^{3+} (0.530 Å)].[47]

The acentric space groups make measurement of the non-linear optical properties[33] an attractive prospect if suitable crystals become available, particularly in the

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case of $[VO][PO_3]_2$. It has recently been shown[48,49] that the non-linear polarisabilities of several iodate crystals may be interpreted in terms of a bond-additivity model where two terms, $\beta^{\parallel}$ and $\beta^{\perp}$, are required to describe the non-linear response of a particular bond. For the iodates the dominant contribution was shown to come from the short I–O bonds and the lone pair on the iodine, and $\beta^{\parallel} : \beta^{\perp}$ was found to be *ca.* 3 : 1. This type of analysis has recently been extended[50] to interpret published data on a large number of oxide systems ABO_x. The ratio $\beta^{\parallel} : \beta^{\perp}$ was found to lie between 3 and 4 : 1 for a wide range of M–O bonds (M = Be, Zn, S, C, N, P, Br, or I), except for M = Ta, Nb, and Ti where the ratio was much higher (*ca.* 10 : 1). For these high-oxidation-state d^0 transition-metal ions, ligand-to-metal π bonding, as well as σ bonding, is thought to be particularly significant, in contrast to the main-group elements where σ bonding is dominant.[51] It appears that the high $\beta^{\parallel} : \beta^{\perp}$ ratio found for Ta–, Nb–, and Ti–O bonds may reflect the π bonding *via* some mechanism and it will be of interest to examine the vanadyl bond in this respect for the interpretation of ligand-field spectra of vanadyl complexes[34,35] invokes significant π bonding in the short V–O bond.

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