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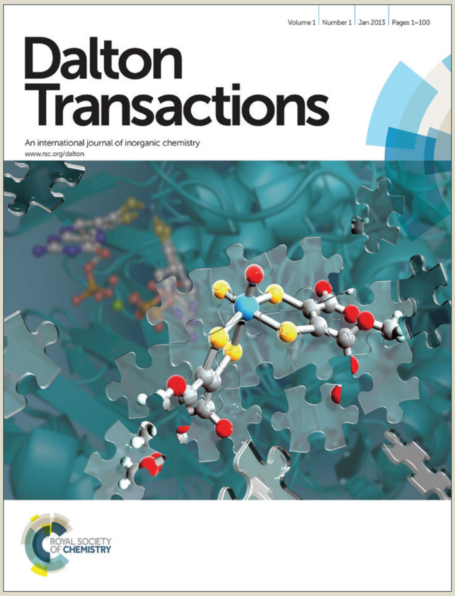

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Di-, Tri- and Tetranuclear Molecular Vanadium Phosphonates: A Chloride Encapsulated Tetranuclear Bowl

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ABSTRACT

The reaction of vanadium(III) trichloride with *tert*-butylphosphonic acid (t-$BuPO_3H_2$) in the presence of 1,10-phenanthroline/2,2′-bipyridine as ancillary ligands in acetonitrile at room temperature afforded, two dinuclear dicationic vanadium(IV) complexes $[(VO)_2(phen)_2\{t\text{-}BuPO_2(OH)\}_2(OH_2)_2]\cdot 2Cl$ [**1**] and $[(VO)_2(bipy)_2\{t\text{-}BuPO_2(OH)\}_2(OH_2)_2]\cdot 2Cl$ [**2**]. On the other hand, when the reaction was carried out in methanol the dinuclear vanadium(V) complex $[(VO)_2(bipy)_2(\mu_2\text{-}O)_2(t\text{-}BuPO_3)_2]\cdot 2CH_3OH\cdot 0.5CH_2Cl_2$ [**3**] was isolated. While **1** and **2** contain two six- membered $V_2P_2O_4$ rings, **3** contains a unique four-membered V_2O_2 ring. Replacement of *tert*-butylphosphonic acid by tritylphosphonic acid ($Ph_3CPO_3H_2$) under the same reaction conditions in methanol leads to the formation of dicationinc trinuclear vanadium(IV) complexes $[(VO)_3(phen)_3(Ph_3CPO_3)_2(OH_2)_3]\cdot CHCl_3\cdot 2(OH)\cdot 2MeOH\cdot 1.5H_2O$ [**4**], and $[(VO)_3(bipy)_3(Ph_3CPO_3)_2(CH_3OH)_3]\cdot 2(OH)\cdot 4CH_3OH\cdot 5H_2O$ [**5**]. In these complexes, the triangular V(IV) platform is held together by two bicapping tripodal phosphonate ligands. Replacement of the chelating 2,2′-bipyridine ligand with 3,5-dimethyl-1*H*-pyrazole, under the same reaction conditions, afforded a tetranuclear vanadium(V) complex $[\{(VO)_4(Ph_3CPO_3Me)_4(\mu\text{-}O)_4\}Cl]\{3,5\text{-}Me_2PzH_2\}\cdot 3C_7H_8\cdot H_2O\cdot CH_3OH$ [**6**]. Remarkably **6** possess a unique bowl-shaped structure encapsulating a chloride anion.

INTRODUCTION

Transition metal phosphonates possessing extended structures[1] have been extensively studied for the last two decades in view of their potential applications in different areas such as cation exchange,[2] NLO materials,[3] luminescence properties,[4] ion sensors,[5] catalysis,[6] catalyst supports,[7] sorption,[8] *etc*. In parallel, there have been continuous efforts for the preparation of molecular metal phosphonates by using various synthetic strategies including the use of sterically bulky phosphonic acids and ancillary ligands.[9] These efforts have resulted in the isolation of molecular transition metal phosphonates of varying nuclearities.[10,9] This remarkable modulation in nuclearity is partly due to the versatile coordination capability of the ligands $[RPO_3]^{2-}$ and $[RP(OH)O_2]^-$ (Chart 1). In contrast to molecular transition metal phosphonates containing Cu(II), Mn(II) or Co(II) those containing V(III), V(IV) or V(V) are still relatively few.[11] Some examples of molecular vanadium phosphonates have been reported by us,[12] Winpenny and coworkers[13], Zubieta and co-workers[14] and Clearfield and co-workers,[15] and some other groups,[16] representative examples of which are shown in the ESI. On the other hand, researchers, particularly Zubieta and co-workers have shown, that the oxovanadium organophosphonate family ($V/O/RPO_3^{2-}$) possessing extended structures has a rich structural chemistry.[17]

Molecular phosphonate chemistry is guided by two important components, one the nature of the phosphonic acid and the other the nature of the co-ligand. In trying to obtain new analogues in the vanadium phosphonate family we used the co-ligands, 1,10-phenanthroline and 2,2′-bipyridine which are known to restrict the nuclearity.[18,9a] On the other hand, we also used 3,5-dimethyl-1*H*pyrazole which has been shown in other instances to afford larger nuclearity aggregates.[19,9a,9b] The phosphonic acids that we employed viz., *tert*-butylphosphonic acid (t-$BuPO_3H_2$) and tritylphosphonic acid ($Ph_3CPO_3H_2$) are sterically encumbered apart from being lipophilic. Accordingly, as described below, in these investigations we were able to isolate and structurally characterize six molecular vanadium phosphonate assemblies [(VO)$_2$(phen)$_2${*t*-BuPO$_2$(OH)}$_2$(OH$_2$)$_2$]·2Cl [**1**], [(VO)$_2$(bipy)$_2${*t*-BuPO$_2$(OH)}$_2$(OH$_2$)$_2$]·2Cl [**2**], [(VO)$_2$(bipy)$_2$(μ_2-O)$_2$(*t*-BuPO$_3$)$_2$]·2CH$_3$OH·0.5CH$_2$Cl$_2$ [**3**], [(VO)$_3$(phen)$_3$(Ph$_3$CPO$_3$)$_2$(OH$_2$)$_3$]·CHCl$_3$·2(OH)·2MeOH·1.5H$_2$O [**4**], [(VO)$_3$(bipy)$_3$(Ph$_3$CPO$_3$)$_2$(CH$_3$OH)$_3$]·2(OH)·4CH$_3$OH·5H$_2$O [**5**] and [{(VO)$_4$(Ph$_3$CPO$_3$Me)$_4$(μ-O)$_4$}Cl]{3,5-Me$_2$PzH$_2$}·3C$_7$H$_8$·H$_2$O·CH$_3$OH [**6**]. All of these compounds have been prepared by *normal* solution synthesis at ambient temperature.

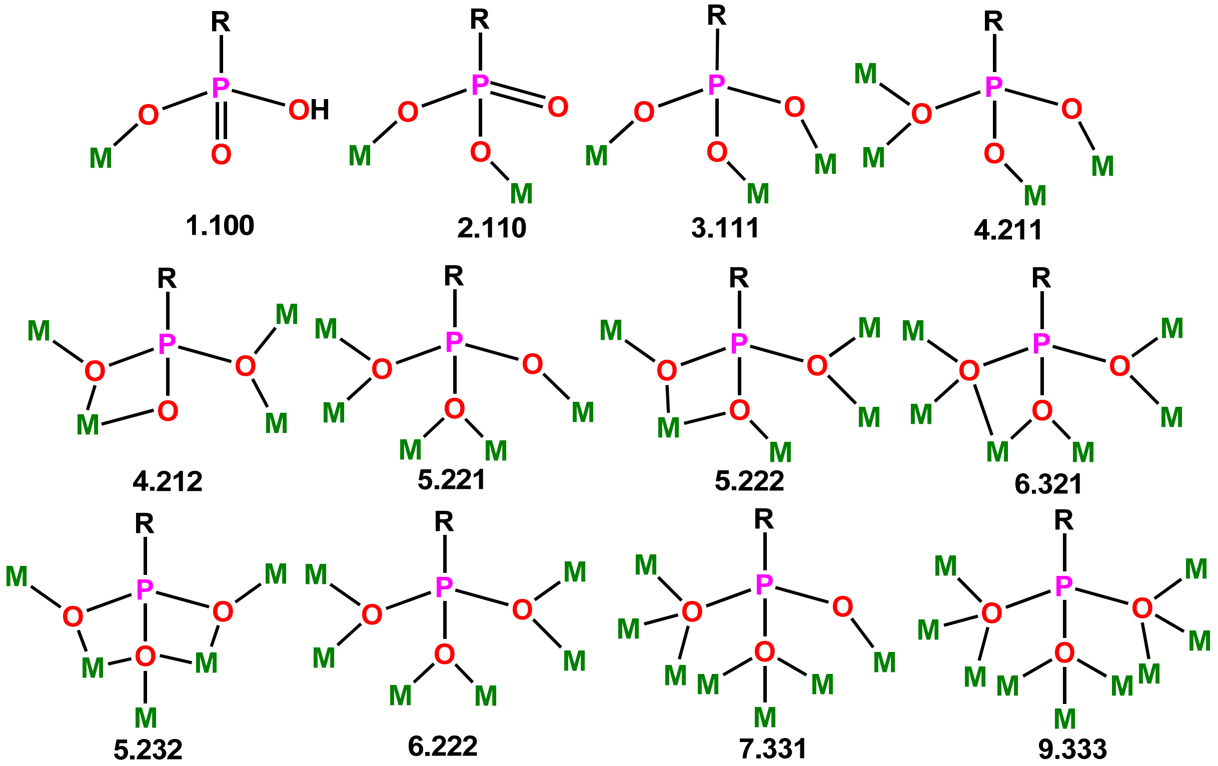


Chart 1. Binding capacity of the phosphonate ligands (Harris notation[20] has been used).

EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[21] The following chemicals were used as obtained:

anhydrous VCl_3 (Lancaster, U.K.), triethylamine (S.D. fine Chemicals, India), $AlCl_3$ (S.D. Fine Chemicals, India), PCl_3 (S.D. Fine Chemicals, India), 2,4-pentanedione (S.D. Fine Chemicals, India), hydrazine hydrate ($N_2H_4 \cdot H_2O$; S.D. Fine Chemicals, India), 1,10-phenanthroline (Aldrich, U.S.A.), 2,2′-bipyridine (Spectrochem, India), acetonitrile (S.D. Fine Chemicals, India) methanol (S.D. Fine Chemicals, India) and toluene (S.D. Fine Chemicals, India) were used as received. 3,5-Dimethyl-1*H*-pyrazole,[22,21a] (trimethyl)phosphonic acid (t-$BuCPO_3H_2$),[23] and tritylphosphonic acid ($Ph_3CPO_3H_2$)[24] were prepared according to the literature procedures.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer Spectrum Version FT IR spectrophotometer operating at 400-4000 cm^{-1}. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadruple mass spectrometer. Thermogravimetric analysis (TGA) (heating rate of 10 ˚C min^{-1}) had been carried out on a Perkin-Elmer Pyris 6 machine.

Synthesis of 1. (Scheme 1). A solution of 1,10-phenanthroline (phen) (0.045 g, 0.250 mmol) and t-$BuPO_3H_2$ (0.017 g, 0.125 mmol) with Et_3N (0.510 g, 0.500 mmol) in CH_3CN (40 ml) were added slowly to a solution of VCl_3 (0.039 g, 0.250 mmol) in CH_3CN (10 ml). The reaction mixture was then stirred for 24 h and filtered. The resulting green colored filtrate was evaporated and was kept for crystallization in CH_3CN/toluene (2:1) mixture. Deep green block-shaped crystals of **1** were obtained after 7-8 days. Yield: 0.045 g, 41 % (based on vanadium). Mp: 135 ˚C (d). Anal. Calcd for $C_{32}H_{40}Cl_2N_4O_{10}P_2V_2$ (**1**; 875.40): C, 43.90; H, 4.61; N, 6.40. Found: C, 43.84; H, 4.65; N, 6.35. IR (KBr, ν/cm^{-1}): 3352 (b, m), 2869 (m), 1643 (w), 1585 (w), 1523 (w), 1463 (m), 1430 (w), 1178 (s), 1142 (m), 1092 (s), 987 (s), 936 (m), 928 (m), 859 (w), 834 (w), 740 (w), 727 (m), 653 (w), 489 (m), 430 (w). ESI-MS (m/z): 976.03 [[$(VO)_2(phen)_2\{t\text{-Bu-}PO_2(OH)\}_2(OH_2)_2$] + 2$Cl^-$ + 2CH_3CN + H_2O + H^+]$^+$ (Fig. 1).

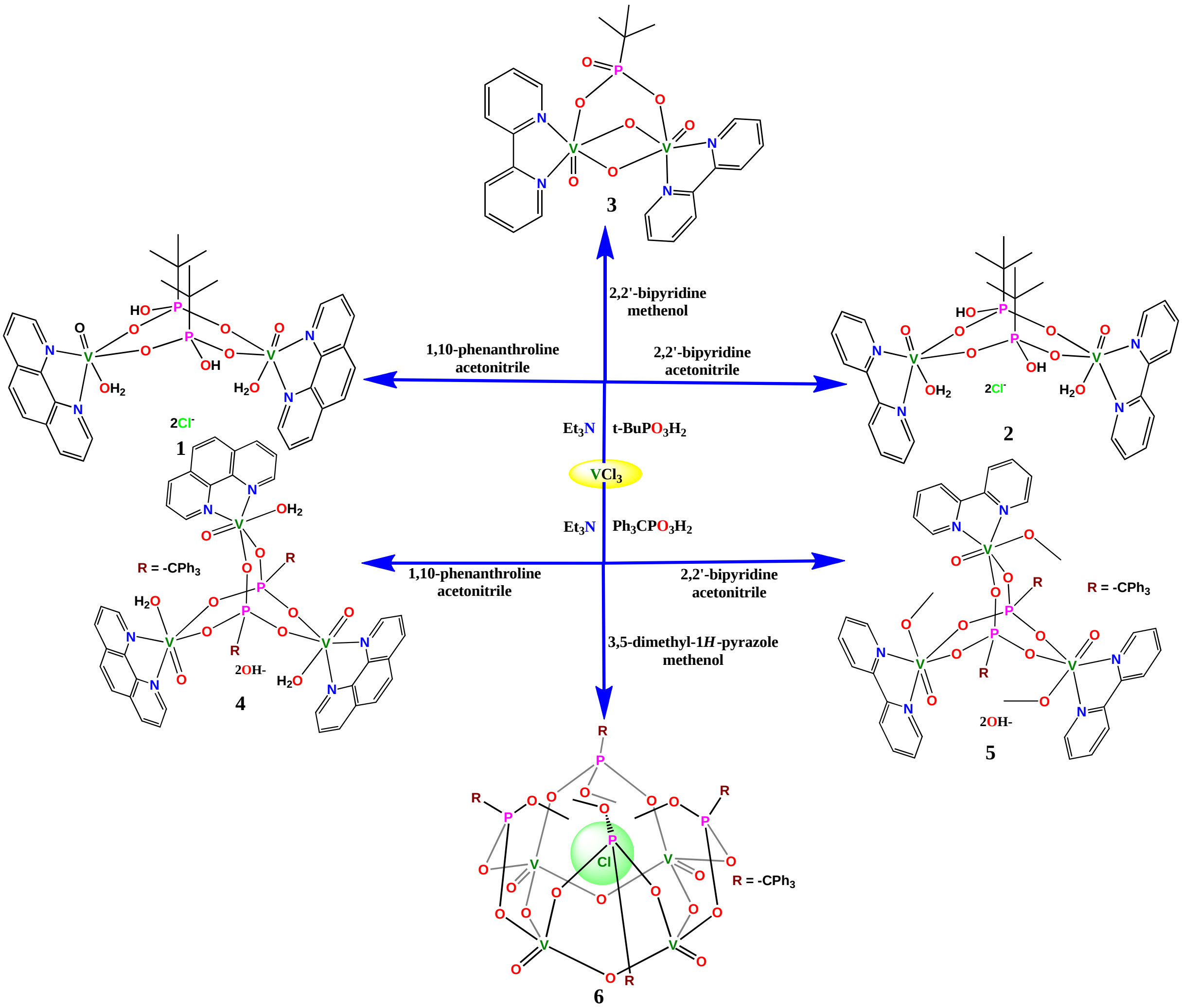
Synthesis of 2. (Scheme 1). A solution of 2,2′-bipyridine (bipy) (0.039 g, 0.250 mmol) and *t*-$BuPO_3H_2$ (0.017 g, 0.125 mmol) and Et_3N (0.510 g, 0.500 mmol) in CH_3CN (40 ml) was added slowly to a solution of VCl_3 (0.039 g, 0.250 mmol) in CH_3CN (10 ml). The reaction mixture was then stirred for 24 h and filtered. The resulting green colored filtrate was evaporated and was kept for crystallization in CH_3CN/toluene (2:1) mixture. Deep green block-shaped crystals of **2** were obtained after 6-7 days. Yield: 0.048 g, 46 % (based on vanadium). Mp: 122 ˚C (d). Anal. Calcd for $C_{28}H_{40}Cl_2N_4O_{10}P_2V_2$ (**2**; 827.36): C, 40.65; H, 4.87; N, 6.77. Found: C, 40.56; H, 4.84; N, 6.69. IR (KBr, *v*/cm^{-1}): 3353 (b, m), 2975 (m), 2677 (m), 2605 (m), 2497 (w), 1611 (m), 1603 (m), 1568 (w), 1498 (w), 1476 (m), 1446 (m), 1396 (w), 1316 (w), 1186 (s), 1173 (s), 1089 (s), 1061 (m), 1034 (m), 985 (s), 923 (m), 832 (w), 772 (m), 735 (m), 661 (m), 566 (w), 490 (m), 417 (w). ESI-MS (m/z): 905.01 [[$(VO)_2(bipy)_2\{t\text{-Bu-}PO_2(OH)\}_2(OH_2)_2$] + 2$Cl^-$ + CH_3CN + 2H_2O + H^+]$^+$ (ESI).

Synthesis of 3. (Scheme 1). A solution of 2,2′-bipyridine (0.0359 g, 0.230 mmol) and *t*-$BuPO_3H_2$ (0.016 g, 0.115 mmol) and Et_3N (0.0469 g, 0.460 mmol) in MeOH (40 ml) were added slowly to a solution of VCl_3 (0.036 g, 0.230 mmol) in MeOH (10mL). The reaction mixture was then stirred for 24 h and filtered. The resulting brown colored filtrate was evaporated and was kept for crystallization in a MeOH/CH_2Cl_2 (1:1) mixture. Green block-shaped crystals of **3** were obtained after 8-10 days.Yield: 0.042 g, 43 % (based on vanadium). Mp: 164 ˚C (d). Anal. Calcd. for $C_{30.5}H_{43}ClN_4O_{12}P_2V_2$ (**3**; 856.97): C, 42.75; H, 5.06; N, 6.54. Found: C, 42.60; H, 5.03; N, 6.48. IR (KBr, *v*/cm^{-1}): 3389 (b, w), 3055 (w), 2960 (m), 2740 (w), 2605 (w), 2497 (m), 2497 (m), 1657 (w), 1601 (s), 1566 (w), 1497 (m), 1474 (s), 1445 (s), 1398 (w), 1314 (m), 1138 (s), 1033 (m), 976 (s), 935 (s), 852 (s), 771 (s), 731 (m), 657 (m), 637 (m), 540 (m), 498 (m), 416 (w). ESI-MS (m/z): 615.04 $[\{(VO)_2(bipy)_2(\mu_2\text{-}O)_2(t\text{-}Bu\text{-}PO_3)_2 + H^+\}]^+$ (ESI). ^{31}P NMR (500 MHz, DMSO-d$_6$): δ 40.12 (s) (ESI).

Synthesis of 4. (Scheme 1). A solution of 1,10-phenanthroline (0.0414 g, 0.230 mmol) and t-BuPO$_3$H$_2$ (0.016 g, 0.115 mmol) and Et$_3$N (0.0469 g, 0.460 mmol) in MeOH (40 mL) were added slowly to a solution of VCl$_3$ (0.036 g, 0.230 mmol) in MeOH (10 mL). The reaction mixture was then stirred for 24 h and filtered. The resulting brown filtrate was evaporated and was kept for crystallization in MeOH/CHCl$_3$ (1:1) mixture. Block-shaped brown crystals of **4** were obtained after 6 days. Yield: 0.038 g, 29 % (based on vanadium). Mp: 155 ˚C (d). Anal. Calcd for $C_{77}H_{74}Cl_3N_6O_{17.5}P_2V_3$ (**4**; 1684.57): C, 54.90; H, 4.43; N, 4.99. Found: C, 54.84; H, 4.48; N, 4.92. IR (KBr, ν/cm^{-1}): 3432 (b, m), 2937 (m), 2739 (m), 2678 (s), 2491 (m), 1626 (m), 1476 (m), 1398 (m), 1193 (s), 1073 (s), 1037 (m), 977 (m), 852 (m), 727 (m), 702 (m), 553 (m). ESI-MS (m/z): 692.58 $[(VO)_3(phen)_3(Ph_3CPO_3)_2]^{2+}$ (ESI).

Synthesis of 5. (Scheme 1). A solution of 2,2′-bipyridine (0.0359 g, 0.230 mmol) and t-BuPO$_3$H$_2$ (0.016 g, 0.115 mmol)and Et$_3$N (0.0469 g, 0.460 mmol) in MeOH (40 ml) were added slowly to a solution of VCl$_3$ (0.036 g, 0.230 mmol) in MeOH (10 ml). The reaction mixture was then stirred for 24 h and filtered. The resulting brown colored filtrate was evaporated and was kept for crystallization in MeOH /CHCl$_3$ (1:1) mixture. Block shaped brown crystals of **5** were obtained after 5-6 days. Yield: 0.041 g, 32 % (based on vanadium). Mp: 124 ˚C (d) Anal. Calcd for $C_{75}H_{94}N_6O_{23}P_2V_3$ (**5**; 1662.37): C, 54.19; H, 5.70; N, 5.06; Found: C, 54.09; H, 5.65; N, 4.98. IR (KBr, ν/cm^{-1}): 3385 (b, m), 2678 (w), 1601 (s), 1574 (w), 1494 (m), 1473 (m), 1444 (s), 1314 (m), 1135 (s), 1096 (s), 1023 (s), 942 (m), 771 (m), 735 (m), 702 (m), 663 (w), 557 (m), 4909 (m), 418 (w). ESI-MS (m/z): 656.88 $[(VO)_3(bipy)_3(Ph_3CPO_3)_2]^{2+}$ (ESI).

Synthesis of 6. (Scheme 1). A solution of 3,5-Me_2PzH (0.039 g, 0.410 mmol) and $Ph_3CPO_3H_2$ (0.266 g, 0.820 mmol)and Et_3N (0.125 g, 1.23 mmol) in MeOH (40 ml) was added slowly to a solution of VCl_3 (0.129 g, 0.820 mmol) in MeOH (10 ml). The reaction mixture was then stirred for 24 h and filtered. The brown colored filtrate was evaporated and was kept for crystallization in a MeOH/toluene mixture. Reddish brown crystals of **6** were obtained after 12-14 days. Yield: 0.044 g, 11 % (based on vanadium). Mp: 132 ˚C (d). Anal. Calcd for $C_{107}H_{111}ClN_2O_{22}P_4V_4$ (**6**; 2140.17): C, 60.05; H, 5.23; N, 1.31; Found: C, 59.98; H, 5.14; N, 1.22. IR (KBr, ν/cm^{-1}): 3385 (b), 3056 (m), 2952 (m), 2852 (m), 1599 (m), 1493 (m), 1445 (m), 1161 (s), 982 (m), 816 (m), 744 (m), 699 (s), 628 (m), 555 (s). ESI-MS (m/z): 1736.52 $[\{[(VO)_4(Ph_3CPO_3Me)_4(\mu\text{-}O)_4]Cl\}^- + H_2O + 2H^+]^+$ (Fig. 3). ^{31}P NMR (500 MHz, DMSO-d_6): δ 25.51 (s) (ESI).



Scheme 1. Syntheses of **1-6**.

X-ray Crystallography. Data were collected on Bruker APEX IICCD diffractometer (MoK$_\alpha$, λ = 0.71073 Å). Complete hemispheres of data were collected using ω-scans (0.3°, up to30 s/frame). Integrated intensities were obtained with SAINT+.[25] For absorption correction SADABS was used.[26] Structure solution and refinement were performed with the SHELXTL.[27] The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2.[28] All the other non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on the carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some solvent molecules could not be modeled satisfactorily because of disorder problem. Therefore the Olex/Mask[29] was used to remove such disordered units from the respective overall intensity data. In compound **2**, two of the carbon atoms of one of the *t*-butyl groups and one of the oxygen atoms of the phosphonate ligand are disordered into two positions in 0.5:0.5 occupancies. The details of the masked electron density have been provided. It is noted that the calculated density values in **4** and **5** assumes values less than 1 and it is due to the large amount of masked electron density. Thermo gravimetric analysis (TGA) of compound **4** show that the initial weight loss value of ~ 12 % below 165 ºC is matching fairly well with the omitted solvents ($1CHCl_3$, 2MeOH, 1.5 H_2O) corresponds to the masked density (12.4 %). In case of compound **5**, weight loss of ~ 12 % is closer to that of the contributions from the solvent molecules (4MeOH, $5H_2O$ molecules) of the masked electron density (13.1 %). Because of relatively poor date quality in case of **6**, the wR_2 is little high. DIAMOND (version 3.1) has been used for mean-plane analyses as well as molecular drawings. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

Squeeze/Mask Details:

Compound **3**

Electron count 33.2 (void of 210.4 Å^3) per unit cell accounts for 0.5 CH_2Cl_2 and 0.5 MeOH molecules [30 total number of calculated e$^-$ (Z=1)]

Compound **4**

Electron count 505.7 (void of 1810.0 Å^3) per unit cell accounts for a $CHCl_3$, 2 methanol and 1.5 water (H_2O) molecules and 2 OH anions [508 total no. of calculated e$^-$ (Z = 4)].

Compound **5**

Electron count 779.6 (void of 1073 Å^3) per unit cell accounts for 4 methanol (CH_3OH) molecule and 2 OH anions and 5 water (H_2O) molecules [780 total no. of calculated e$^-$ (Z = 6)].

Compound **6**

Electron count 349.1 (void of 584.9 Å^3) per unit cell accounts for 1 methanol molecule and 2.5 water molecules [344 total no. of calculated e$^-$ (Z = 8)].

RESULTS AND DISCUSSION

Synthesis

As mentioned earlier, molecular vanadium phosphonates are relatively sparse in comparison to other transition metal phosphonates, such as copper(II) phosphonates.[9a] The higher nuclearity molecular vanadium phosphonates include $[H_6(VO_2)_{16}(MePO_3)_8](Me_4N)_8$ [16b] T $[V_{14}O_{22}(OH)_4(H_2O)_2(C_6H_5PO_3)_8]\cdot 2Cl\cdot 2NH_4$ (ESI)[14c], $[V^{III}{}_{12}(V^{IV}O)(\mu_3\text{-}OH)4(\mu_2\text{-}OH)_8(\mu_2\text{-}OEt)_4(EtOH)_4\text{-}(PhCO_2)_4(t\text{-}BuO_3P)_8]Cl_2$[13], $[H_{12}(VO_2)_{12}(PhPO_3)_8][N(C_3H_7)_4]_4$ [16a] and $[V_{11}(O)_{12}(EtO)_{13}(EtOH)(Ph_3CCO_2)_2(MePO_3)]\cdot EtOH$.[11b] Among the hexanuclear family, the following members are known: $[(VO)_6(PhPO_3)_8]_4Cl$ (ESI),[14a] $[V^{III}{}_6(\mu_3\text{-}O)_2(O_2CtBu)_8(t\text{-}BuCO_2H)_2(t\text{-}BuPHO_3)_2(t\text{-}BuPO_3)_2$ and $[V^{V}{}_6O_{12}(H_2O)_3(Ph_2CHPO_3)_3]$ (ESI)[15]. Only one pentanuclear derivative viz., $V^{III}{}_5(\mu_3\text{-}OH)(t\text{-}BuO_3P)_6Cl_2(py)_6$ is known (ESI).[13] Winpenny and coworkers reported a tetranuclear vanadium(IV) phosphonate, $[V_4(O)(Ph_3CPO_3)_4Py_4]$.[13] Our research group has previously reported two distorted double-four-ring (D4R) cubic tetranuclear vanadium (IV) phosphonate cages $[(VO)_4(3,5\text{-}Me_2PzH)_8(CCl_3PO_3)_4]$ and $[(VO)_4(3,5\text{-}Me_2PzH)_4\text{-}$

(t-$BuPO_3$)$_4$] in the reaction of VCl_3 with t-$BuPO_3H_2$ or $Cl_3CPO_3H_2$ using 3,5-dimethyl-1*H*-pyrazole as the co-ligand.[12,30] In these compounds, V(IV) ions and phosphorus atoms occupy alternate corners of the distorted cube (ESI). From the search of the literature it is clear that low-nuclearity vanadium phosphonates (nuclearity less than 4) are absent. We have previously shown, in the case of Cu(II) phosphonates that chelating ancillary ligands such as 1,10-phenanthroline or 2,2′-bipyridine are effective in affording low-nuclearity complexes.[9a,18]

Accordingly, in the current study we observe the formation of compounds **1-3** which are dinuclear, and compounds **4** and **5** which are trinuclear, when 1,10-phenanthroline or 2,2′-bipyridine are used as ancillary ligands (Scheme 1). On the other hand the reaction of VCl_3 with $Ph_3CPO_3H_2$ in the presence of 3,5-dimethyl-1*H*-pyrazole afforded the bowl shaped tetranuclear compound, **6.** Remarkably here 3,5-dimethyl-1*H*-pyrazole does not coordinate to the metal center but it assists crystallization through supramolecular interactions. ESI-MS studies indicate that all the compounds (**1-6**) retain their structural integrity under these conditions (see Fig. 1 for a representative mass spectrum; the rest are given in ESI).

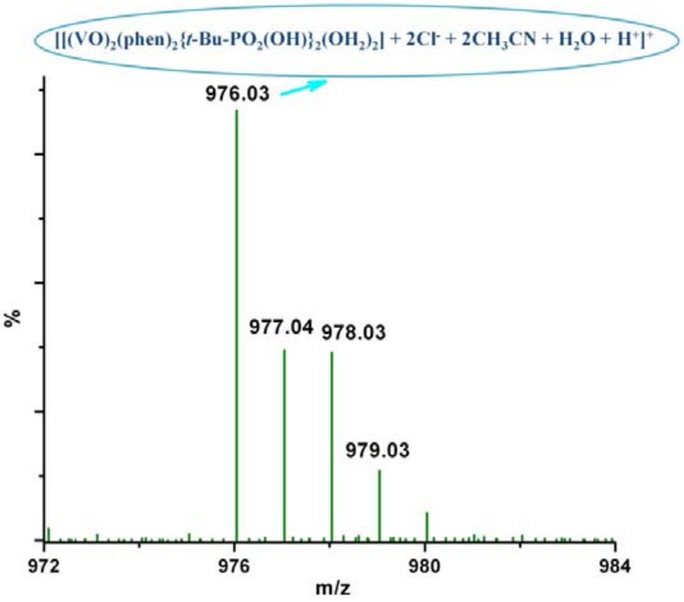


Fig. 1 ESI-MS of **1**.

Molecular Structures of 1-6.

The molecular structures of **1-6** were determined by X-ray crystallography. The crystallographic parameters of these compounds are given in Tables 1-2. CCDC reference numbers for **1-6** are CCDC 990482-990487 respectively.

Table 1. Crystal data and structure refinement parameters of **1-3** (CCDC 990482-990484).

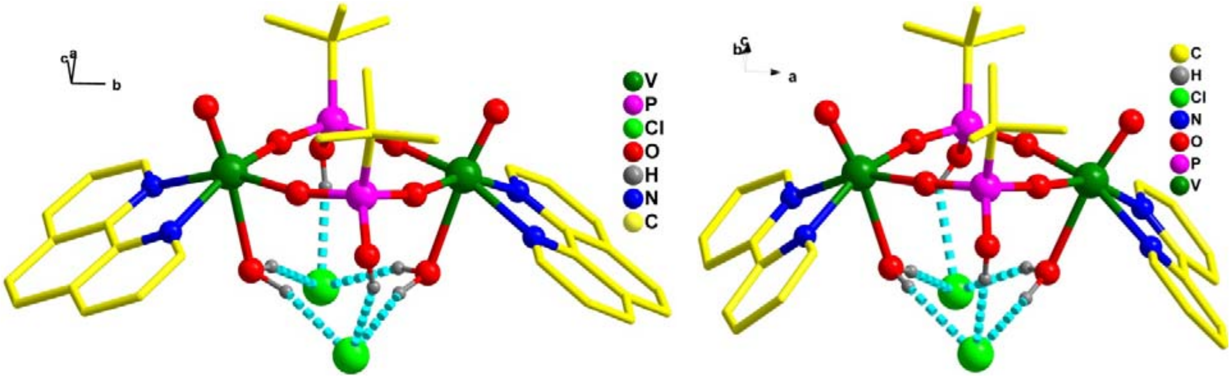
	1	**2**	**3**
Empirical formula	$C_{32}H_{40}Cl_2N_4O_{10}P_2V_2$	$C_{28}H_{41}N_4O_{11}P_2Cl_2V_2$	$C_{51}H_{62}N_8O_{17}P_2V_4$
Formula weight	875.40	844.37	1324.78
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*P*nma	*P*nma	*P*-1
Unit cell dimensions	a = 19.079(5) Å $\alpha = 90^\circ$	a = 23.066(5) Å $\alpha = 90^\circ$	a = 9.765(5) Å $\alpha = 66.947(5)^\circ$
	b = 18.583(5) Å $\beta = 90^\circ$	b = 14.961(5) Å $\beta = 90^\circ$	b = 12.448(5) Å $\beta = 84.914(5)^\circ$
	c = 10.924(5) Å $\gamma = 90^\circ$	c = 10.893(5) $\gamma = 90^\circ$	c = 14.734(5) Å $\gamma = 80.991(5)^\circ$
Volume	3873(2) Å^3	3759(2) Å^3	1626.9(12) Å^3
Z	4	4	1
Density (calculated)	1.501 Mg/m^3	1.492 Mg/m^3	1.352 Mg/m^3
Absorption coefficient	0.761 mm^{-1}	0.783 mm^{-1}	0.673 mm^{-1}
F(000)	1800	1740	682
Crystal size	0.084 x 0.082 x 0.080 mm^3	0.092 x 0.086 x 0.082 mm^3	0.068 × 0.062 × 0.060 mm^3
Theta range for data collection	2.19 to 25.50 deg.	4.08 to 25.4 deg.	4.2 to 25.03 deg.
Index ranges	$21 \leq h \leq 23$ $-21 \leq k \leq 22$ $-13 \leq l \leq 12$	$-27 \leq h \leq 27$ $-17 \leq k \leq 18$ $-13 \leq l \leq 9$	$-12 \leq h \leq 12$ $-16 \leq k \leq 16$ $-19 \leq l \leq 14$
Reflections collected	19242	19194	10470
Independent reflections	3652 [*R(int)* = 0.1282]	3570 [*R(int)* = 0.0585]	5608[*R(int)* = 0.0402]
Completeness to theta = 25.27°	98.0 %	100 %	98.2 %
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	1.0 and 0.078	1.0 and 0.5	1.0 and 0.40

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3652 / 0 / 255	3570/95/252	5608/121/385
Goodness-of-fit on *F2*	1.055	1.034	1.069
Final R indices [I>2sigma(I)]	R_1= 0.0673, wR_2 = 0.1543	R_1 = 0.1182, wR_2 = 0.2723	R_1 = 0.0967, wR_2 = 0.2693
R indices (all data)	R_1 = 0.0898, wR_2 = 0.1670	R_1 = 0.1351, wR_2 = 0.2865	R_1 = 0.1292, wR_2 = 0.3054
Largest diff. peak and hole	1.08 and -1.52 e. Å^{-3}	2.29 and -1.25 e. Å^{-3}	1.48 and -0.80 e. Å^{-3}

Table 2. Crystal data and structure refinement parameters of **3-6** (CCDC 990485-990487).

	4	**5**	**6**
Empirical formula	$C_{74}H_{60}N_6O_{14}P_2V_3$	$C_{71}H_{66}N_6O_{12}P_2V_3$	$C_{212}H_{212}N_4O_{40}P_8Cl_2V_8$
Formula weight	1440.04	1410.05	4182.02
Temperature	100(2) K	100(2) K	100 (2) K
Wavelength	0.71069 Å	0.71069 Å	0.71073 Å
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	C_2/m	*R*-3	*P*2$_1$/n
Unit cell dimensions	a = 26.464(5)Å α =90 °	a = 17.454(3) Å α = 90 °	a = 16.502(17)Å α = 90°
	b = 27.628(5)Å β = 91.213(5)°	b = 17.454(3) Å β = 90 °	b = 32.938(3) Å β = 98.390(2)°
	c = 14.057(5)Å γ = 90 °	c = 45.618(3) Å γ = 120 °	c = 39.238(4) Å γ = 90°
Volume	10275(5)Å^3	12035(4) Å^3	21099(4) Å^3
Z	4	6	8
Density (calculated)	0.931 Mg/m^3	1.167 Mg/m^3	1.317 Mg/m^3
Absorption coefficient	0.343 mm^{-1}	0.438 mm^{-1}	0.496 mm^{-1}
F(000)	2964	4374	8680
Crystal size	0.088 × 0.082 × 0.078 mm^3	0.078 x 0.074 x 0.070 mm^3	0.088 x 0.080 x 0.071 mm^3
Theta range for data collection	2.07 to 25.5 deg.	2.24 to 25.50 deg.	1.85 to 25.50 deg.
Index ranges	$-32 \le h \le 31$ $-33 \le k \le 29$ $-13 \le l \le 17$	$-23 \le h \le 21$ $-21 \le k \le 23$ $-38 \le l \le 60$	$-20 \le h \le 20$ $-40 \le k \le 35$ $-48 \le l \le 42$
Reflections collected	27622	26835	121159
Independent reflections	9723 [*R*(int) = 0.0793]	4973 [*R*(int) = 0.0952]	39165 [*R(int)* = 0.1248]
Completeness to theta = 25.27°	99.5 %	99.9 %	99.80 %
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	1.0 and 0.38	1.0 and 0.59	1.0 and 0.57

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9723/30/452	4973/9/287	39165/264/2455
Goodness-of-fit on F2	1.056	1.055	0.954
Final R indices [I>2sigma(I)]	$R_1 = 0.1178$, $wR_2 = 0.3110$	$R_1 = 0.0669$, $wR_2 = 0.1823$	$R_1 = 0.0948$, $wR_2 = 0.2280$
R indices (all data)	$R_1 = 0.1673$, $wR_2 = 0.3459$	$R_1 = 0.0900$, $wR_2 = 0.1968$	$R_1 = 0.1961$, $wR_2 = 0.2793$
Largest diff. peak and hole	1.24 and -0.85 e.Å^{-3}	0.98 and -0.53 e.Å^{-3}	0.099 and -0.52 e. Å^{-3}

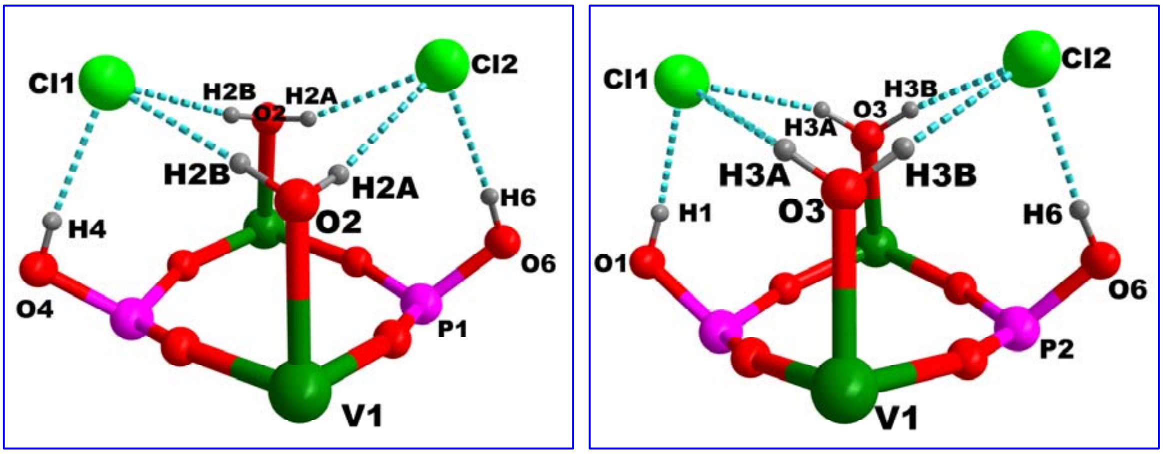


(a) (b)

Fig. 2 Molecular structure of **(a) 1** and **(b) 2**. Some hydrogen atoms and the solvent molecules have been removed for clarity.

X-ray crystallography reveals that molecular structures of **1** and **2** are similar (Fig. 2a and 2b). Both are dinuclear dicationic complexes and contain two chloride (Cl^-) counter anions. The oxidation state of all the vanadium centers is +4 as corroborated from BVS calculations[31] (ESI). The structure of these complexes reveals the presence of two vanadium centers that are bridged to each other by two [*t*-BuP(OH)(O)$_2$]$^-$ ligands. Each V(IV) has a chelating ligand (phen or bipy) along with an oxo group and a coordinated water molecule. Thus, each V(IV) is hexacoordinate (4O, 2N) in an octahedral geometry (ESI). The uncoordinated P-O bond distance [~1.577 (compound **1**) and ~1.530 Å (compound **2**)] is larger than the coordinated P-O bond distance

[~1.498 (compound **1**) and ~1.453 Å (compound **2**)]. The bridging coordination action of the two monoanionic ligands $\{t\text{-BuP(OH)O}_2\}^-$ {Harris Notaion: 2.110} results in an eight-membered ($V_2P_2O_4$) puckered ring where the phosphorous atoms (P) are displaced (0.28 Å) above the mean plane; the vanadium atoms are present below the mean plane position (0.053 Å) (ESI). The two *t*-Bu groups of the phosphonate ligands are present on the same side of the ring. Also, the two V=O motifs are *cis* w.r.t to each other and are present on the same side as the phosphonate ligands. Interestingly, the two chloride counter anions are held together tightly to the dicationic complex through strong hydrogen bonding interactions with the coordinated water molecules and the P-OH units. Thus, each chloride anion is involved in three hydrogen bonding interactions resulting in a bowl-shaped architecture (Fig. 3a and 3b, and ESI). The complete hydrogen bonding interactions present in this compound leads to the generation of an aesthetically pleasing supramolecular architecture (ESI).



(a) (b)

Fig. 3 Bowl-shaped core, formed by H-bonding interactions, of **(a) 1 (b) 2** (Hydrogen bond parameters have been provided in the ESI).

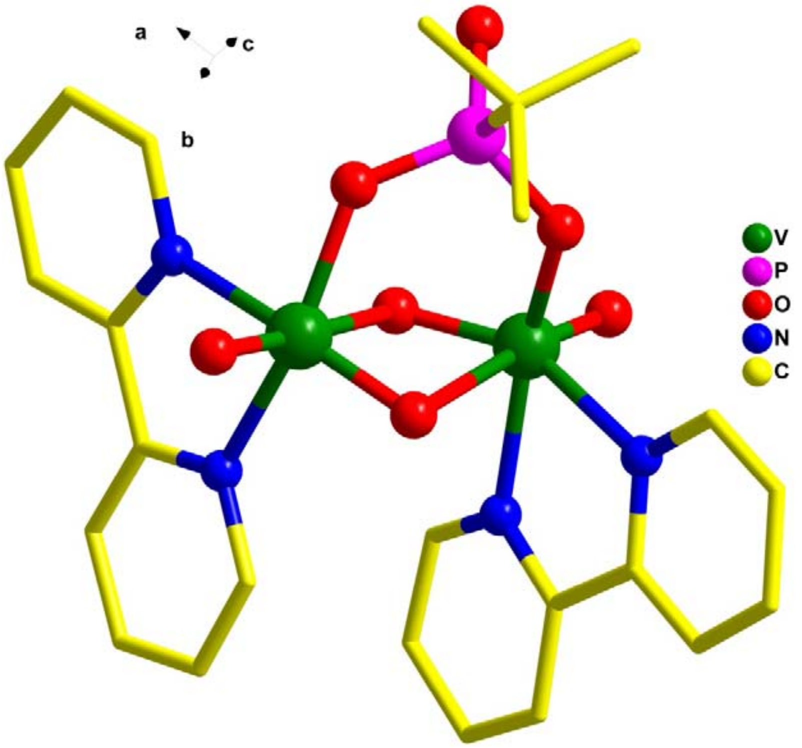


Fig. 4 Molecular structure of **3**. All the hydrogen atoms and the solvent molecules have been removed for clarity.

The molecular structure of **3** also reveals that it is dinuclear (Fig. 4). However, in contrast to **1** and **2,** in **3** the two V centers are in a +5 oxidation state. This structural motif is unique among all vanadium phosphonates. The four-membered V_2O_2 ring is puckered and is supported by a phosphonate ligand**.** The P-O distances involved are 1.553(4) and 1.560(5) Å. **3** is a vanadium dimer containing 2,2′-bipyridine as the ancillary ligand (Fig. 6). Here the two vanadium centres are bridged through a *t*-$BuPO_3^{2-}$ and two O^{2-} ligands. The V-O bonds involved in the V_2O_2 four-membered ring are vastly different: [V1-O3, 1.670(4) Å; V1-O4, 2.335(4) Å; V2-O2, 1.621(5); V2-O3, 2.432(4) Å] indicating V1-O2 and V2-O3 to be weak bonds (Fig. 5).

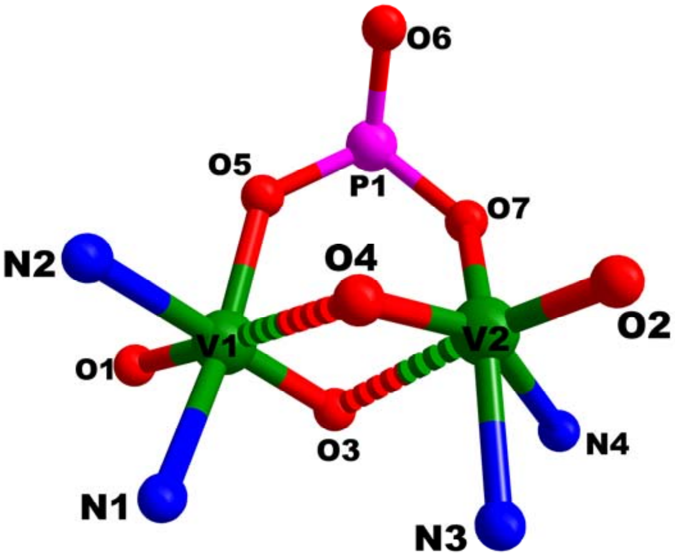
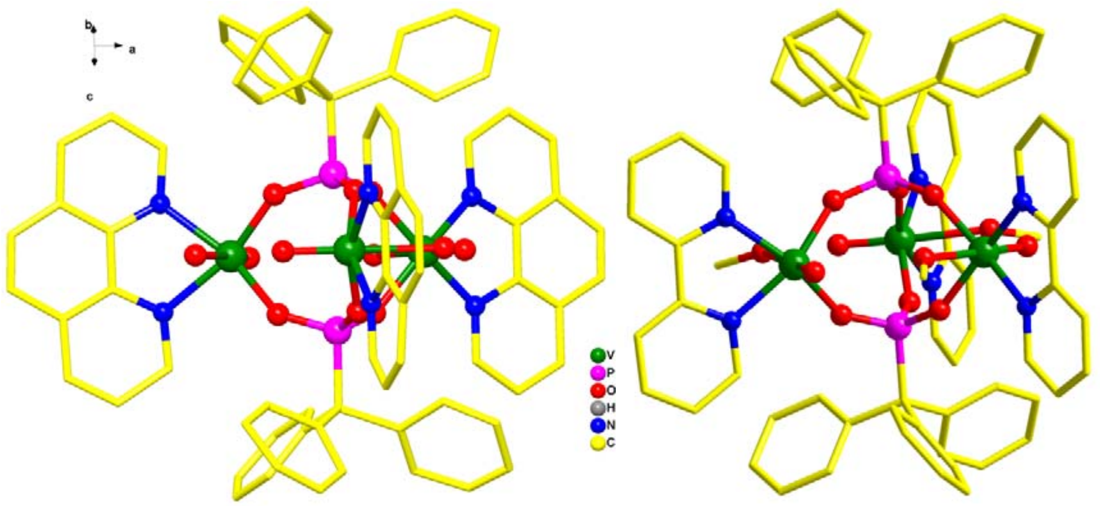


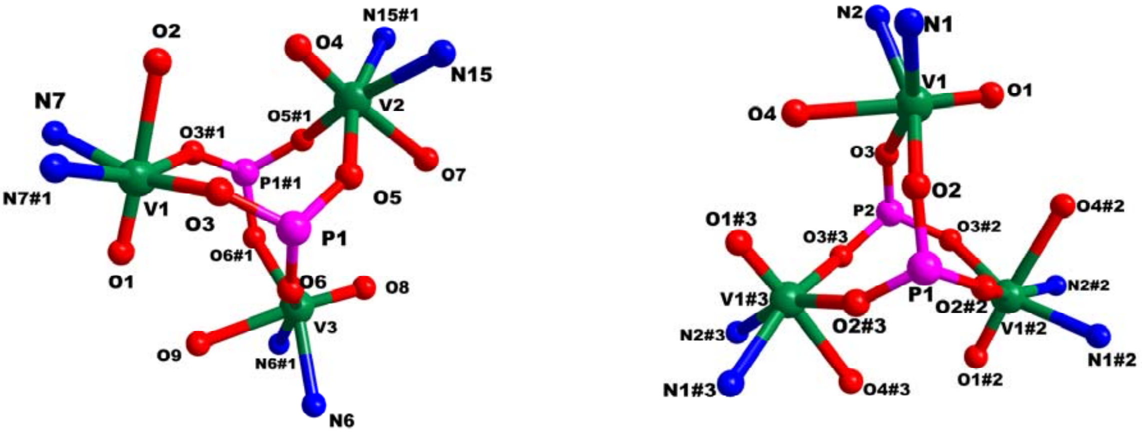
Fig. 5 The dinuclear core of **3**. Important bond distances (in **Å**) and angles (in **º**): V1-O1, 1.624(4); V1-O3, 1.670(4); V1-O4, 2.335(5); V1-N1, 2.130(6); V1-N2, 2.207(6); V2-O2, 1.621(5); V2-O3, 2.432(5); V2-O4, 1.652(5); V2-O7, 1.929(5); V2-N3 2.141(6); V2-N4, 2.217(6); P1-O5 1.553(5); P1-O6, 1.498(5); P1-O7 1.558(5); O1-V1-O3, 107.1(2); O3-V2-O4, 77.8(2); V1-O3-V2, 96.3(2); V1-O4-V2, 100.6(2); V1-O5-P1, 131.2(3); P1-O7-V2 126.5(3); O5-P1-O7, 109.6(3).



(a) (b)

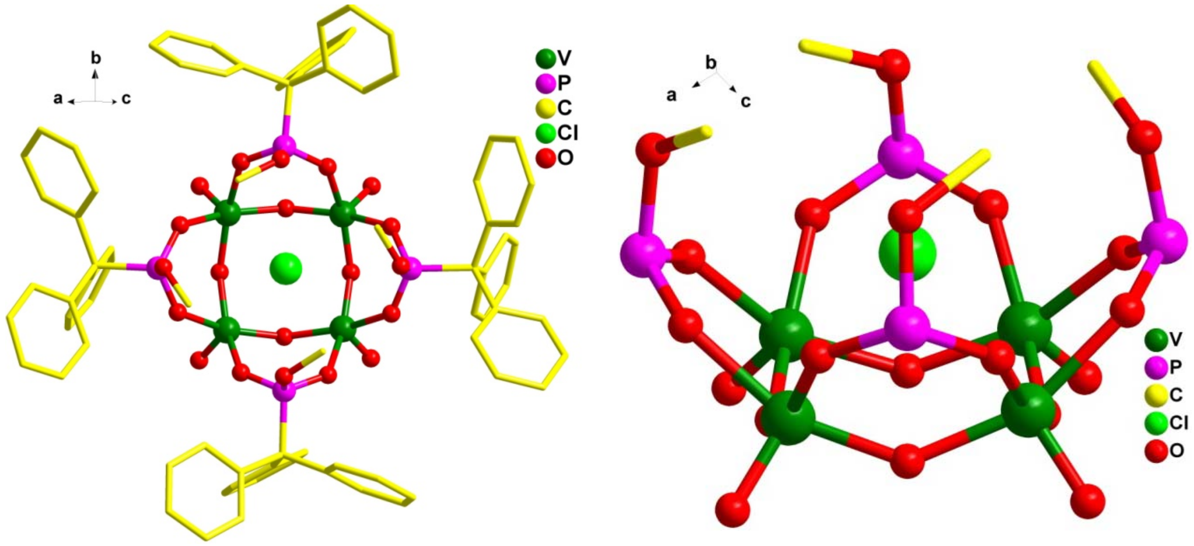
Fig. 6 Molecular structures **(a) 4** and **(b) 5**. Some hydrogen atoms and all the solvent molecules have been removed for clarity.

Compounds **4** and **5** are trinuclear and possess similar structures (Fig. 6a and 6b). All the three V(IV) centers are six-coordinate (2N,4O) in an octahedral geometry. Two hydroxide (OH^-) counter anions balance the charge. These dicationic clusters are also stable under the ESI-MS ESI-MS conditions (ESI). **4** and **5** contain a bicyclic $V_3P_2O_6$ ring system (Fig. 7a and 7b) where a triangular V(IV) platform is held together two bicapping tripodal phosphonate ligands. The only structural difference between them is that in case of **4**, the vanadium centers are coordinated to water molecules whereas in the case of **5**, neutral methanol molecules are attached. Similar kind of cores have been reported for Mn(III) phosphonates,[32] Zn(II) phosphates[33] and Cu(II) phosphonates[34] (ESI) but these are uncommon among the vanadium phosphonates.



(a) (b)

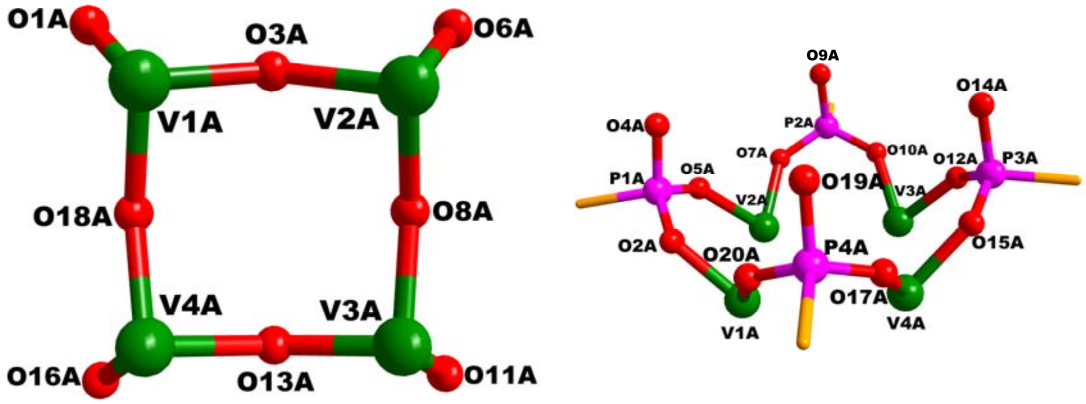
Fig. 7 The $V_3P_2O_6$ core of **(a) 4** and **(b) 5**. Selected bond distances (**Å**) and angles (˚) of **4**: V1-O1, 1.593(6); V1-O3, 1.967(4); V1-N7, 2.101(5); V2-O4, 1.617(6); V2-O5, 1.951(4); V2-N15, 2.107(6); V3-O8, 1.595(7); V3-O6, 1.945(4); V3-N6, 2.126(5); P1-O3, 1.514(4); P1-O5, 1.521(4); P1-O6, 1.526(4); O3-V1-O3$^{\#1}$, 94.1(2); O3-V1-O2, 80.49(15); O1-V1-O3, 101.01(18); O1-V1-N7, 97.4(2); P1-O3-V1, 141.5(2); P1-O5-V2, 139.7(2); P1-O6-V3, 143.6(2); P2-O6-V3, 140.2(3); O5-P1-O6, 111.5(2); O3-P1-O6, 113.0(2); O3-P1-O5, 111.5(2). Selected bond distances (**Å**) and angles (˚) of **5:** V1-O1, 1.589(7); V1-O2, 1.949(7); V1-O3, 1.952(7); V1-O4, 2.321(6); V1-N1, 2.096(9); V1-N2, 2.119(8); P1-O2, 1.525(6); P2-O3, 1.532(6); P1-O2-V1, 147.2(4); P1-O3-V1, 145.3(4); O2-V1-O3, 95.3(3); O2-V1-O4, 78.8(3); O3-V1-O4, 82.0(3); O2-P1-O2$^{\#2}$, 112.0(3); O2-P1-O2$^{\#3}$, 112.0(3); O2$^{\#2}$-P1-O2$^{\#3}$, 112.0(3); O3-P2-O3$^{\#2}$, 112.3(3); O3-P2-O3$^{\#3}$, 112.0(3); O3$^{\#2}$-P2-O3$^{\#3}$, 112.0(3). Symmetry transformations used to generate equivalent atoms: #1 +X,1-Y,+Z; #2 -Y,-1+X-Y,+Z; #3 1+Y-X,-X,+Z



(a) (b)

Fig. 8 (a) Molecular structure of **6**. Hydrogen atoms and the solvent molecules have been removed for clarity. **(b)** The core of **6** showing the bowl-shaped core encapsulating the chloride ion. The trityl group of the phosphonate, some hydrogen atoms and the solvent molecules have been removed for clarity.

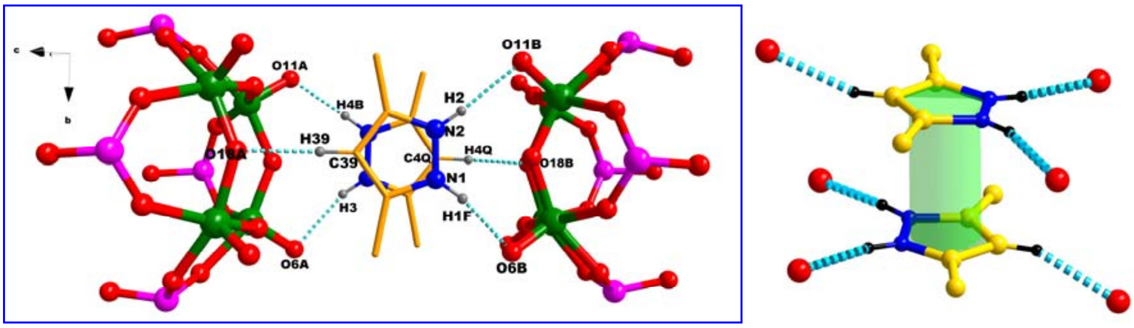
The X-ray crystallographic analysis of the complex **6** shows that it is a tetranuclear bowl shaped V(V) aggregate (Fig. 8). The metal assembly is enclosed by a lipophilic organic sheath composed of trityl groups which are attached to the phosphonate ligands. The presence of protonated 3,5-DMPzH_2 makes the bowl shape aggregate negatively charged. The tetranuclear aggregate is formed as a result of the cumulative coordination action of four $[Ph_3CPO_2(OCH_3)]^-$ ligands which are generated in situ. The base of the complex contains a $[V_4O_4]$ square (V---V distance, ~ 3.4 Å) (Fig. 9a). Four V=O units, serve as *legs* to the square-base of the compound. On the other hand, four $[PO_3]$ units emanate from the base and provide an encapsulating surface, within which is trapped a chloride ion (Fig. 8b) which is placed symmetrically w.r.t all the vanadium and oxygen atoms. The V(V)-Cl$^-$ distances are smaller (average 3.00 Å) than the sum of the van der Waals distance of V(V) and Cl$^-$ (3.85 Å).[35] Previously bowl-shaped vanadates with a V_4O_4 core are known, however, all of these contain carboxylate ligands and none contains phosphonate or phosphinate ligands.[36]



(a) (b)

Fig. 9 (a) Tetranuclear square-base **6** **(b)** The four phosphonate ligands emerging from the square-base of **6**. Important bond distances (**Å**) and angles (in **°**): V1A-O1A, 1.576(5); V1A-O2A, 1.941(5); V1A-O3A, 1.796(5); V1A-O18A, 1.878(5); V1A-O20A, 1.984(5); V2A-O3A, 1.848(5); V2A-O5A, 1.985(5); V2A-O5A, 1.985(5); V2A-O6A, 1.597(5); V2A-O7A, 1.974(5); V2A-O8A, 1.802(5); V3A-O8A, 1.847(5); V3A-O10A, 1.993(5); V3A-O11A, 1.592(5); V3A-O12A, 1.946(5); V3A-O13A, 1.806(5); V4A-O13A, 1.835(5); V4A-O15A, 1.835(5); V4A-O16A, 1.585(5); V4A-O17A, 1.966(5); V4A-O18A, 1.818(5); O1A-V1A-O3A, 102.3(2); O1A-V1A-O18A, 100.9(2); O3A-V1A-O18A, 94.1(2); O2A-V1A-O20A, 82.82(19); V1A-O3A-V2A, 135.8(3); V1A-O18A-V3A, 137.1(3); V2A-O8A-V3A, 136.2(3); V3A-O13A-V4A, 136.4(3).

Another interesting feature of the structure of **6** is that supramolecular interactions between two dimethylpyrazolium cations (π---π stacking: ~3.48 Å) as well with V=O generates an octanuclear aggregate (Fig. 10 and ESI). Two face to face bowls interact with each other affording the oval eight-metal ensemble. In **6**, as may be noted, the ancillary ligand does not coordinate to the metal centers but helps in crystallization through supramolecular interactions (Fig. 10).



(a) (b)

Fig. 10 (a) Supramolecular interactions in **6**. The average V=O---H-N distance 2.08 Å (ESI); **(b)** π–π stacking interaction between protonated 3,5-Me_2PzH (π–π distance 3.48 Å).

Summary

In summary, we report six molecular vanadium phosphonates whose nuclearity varies from 2 to 4. Use of 1,10-diphenanthroline and 2,2′-bipyridine as co-ligand afford di- and trinuclear derivatives. 3,5-Dimethylpyrazole, does not bind to the metal centers. However, its protonoated form assists the formation of a supramolecular aggregate in **6**.

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ASSOCIATED CONTENT

Electronic Supplementary Information (ESI). Crystallographic information files (CIF), CCDC 990482-990487 for **1-6**, tables of bond distance (**Å**) and bond angle (˚), coordination environments of the metal centers, TGA plots, Charts S1-S2, Fig. S1-S22 and Tables S1-S15.

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For TOC

Di-, Tri- and Tetranuclear Molecular Vanadium Phosphonates: A Chloride Encapsulated Tetranuclear Bowl

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