



Bimetallic Frameworks

Rational Design of Two-Dimensional Bimetallic Wave Structures from Zigzag Chains via Site-Specific Coordination around the 2,6-Naphthalenediphosphonic Acid Motif

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Abstract: We report the synthesis of a novel aromatic 2,6-naphthalenediphosphonic acid (2,6-NDPA-H₄) and the rational design of molecular, one-, two-, and three-dimensional structures of the resulting copper organophosphonate materials: $[{Cu(terpy)}(2,6-NDPA-H_3)][{Cu(terpy)}(2,6-NDPA-H_3)(2,6-NDPA-H_2)]\cdot 3H_2O$ (2), $[{Cu(terpy)}VO_2(2,6-NDPA-H)]\cdot H_2O$ (4), $[{Cu$

Introduction

A fascinating characteristic of metal-organophosphonate chemistry (MOP) is the remarkable structural diversity observed within this system.^[1] This rich structural diversity introduces a wide range of functions into MOP compounds including sorption, catalysis, ion exchange, intercalation, bone regeneration etc.^[2] Although it is exciting to have such extensive structural variation, this diversity should be controllable to produce predictable metal organic structures. A few examples of isoreticular expansions of organophosphonate metal-organic frameworks (MOFs) have been described to date, using H₂O₃PCH₂-NR-CH₂PO₃H₂ types of bridging units.^[1d,3] Although these reports suggest that MOPs could be novel platforms for catalysis and the design of robust void spaces, the development of new methodologies for constraining structural complexity by engineering metal oxidation states, coordination preferences, structures of the bridging ligand, organophosphonate coordination

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(terpy)}VO₂(2,6-NDPA-H)] (**3**) and [{Cu(H₂O)}(NDPA)_{0.5}] (**1**). Engineering the copper coordination sphere and pH-controlled phosphonate protonation enabled the site specific dimensional evolution of Cu^{II}-organophosphonate frameworks exploiting the deprotonated phosphonate oxygen arms.

modes and protonation states remains relatively unexplored. One important step towards this goal is to improve the current organophosphonate library and to observe the coordination behavior with respect to various metal centers. Very recently, aromatic tetraphosphonic acids, 1,5- and 1,4-naphthalenediphosphonic acids and 2,7-fluorenonediphosphonic acids have been reported.^[1c,4] Surprisingly, the synthesis of another extremely fundamental ditopic bridging ligand, 2,6-NDPA-H₄, has not been reported previously.

In the course of detailed investigations into MOP materials, we synthesized a novel aromatic phosphonate using 2,6-NDPA-H₄ as a linker to the primary metal node and investigated its role in bonding to a organoimine-free copper center. Furthermore, we used the 2,2':6',2"-terpyridine ligand to engineer the coordination environment of the copper center to produce a predefined square pyramidal {Cu(terpy)}²⁺ structural element that limits the spatial expansion so that we could compare the behavior of the organoimine-free Cu^{II} with the constrained {Cu(terpy)}²⁺-organophosphonate compounds, where the square pyramidal {Cu(terpy)}²⁺ has only two available sites for phosphonate coordination. In addition, introduction of the secondary V-P-O subunit can enhance dimensional flexibility and functionality in the constrained {Cu(terpy)}²⁺-organophosphonate compounds. It is noteworthy that V-P-O compounds represent a particularly interesting family of inorganic oxides possessing diverse applications including, most notably, the selective air oxidation of butane to maleic anhydride.^[5] The structural diversity of such vanadate-based materials is related to the ability of vanadium to adopt multiple oxidation states, most commonly between +2 and +5. Each vanadium oxidation state may produce various coordination numbers and form interesting molecular clusters as well as coordination polymers with 1-D, 2-D and 3-D connectivities.^[1,6] Since the judicious choice of reaction conditions dictates the degree of phosphonate protonation^[7] this strategy could be exploited to produce 3-D

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Figure 1. Perspective views of the five Cu-organophosphonates (1, 2a, 2c, 3, and 4) showing their structural evolution.

Results and Discussion

The synthetic procedures for the 2,6-naphthalenediphosphonic acid and complexes **1–4** are shown in Schemes 1 and 2, respectively.



naphthalene-2,6-diylbis(phosphonic acid)

Scheme 1. Synthetic pathway for the preparation of 2,6-naphthalenediphosphonic acid.

Complex **1** (Figure 2) was synthesized hydrothermally at 180 °C. This complex exhibits a 3-D pillared layered structure (Figure 3), where the distorted square pyramidal $\{Cu(H_2O)\}^{2+}$ is connected to fully deprotonated 2,6-NDPA at four of its coordination sites. The coordination modes of NDPA-H₄ observed in this study are summarized in Scheme 3. The maximum binding capacity of the NDPA-H₄ has been reached in complex **1**. The fifth site in the basal plane is occupied by a water molecule.





Scheme 2. Synthetic pathway for the preparation of complexes 1–4. (a) 2,6-naphthalenediphosphonic acid (2,6-NDPA-H₄); (b) 2,2':6',2''-terpyridine.

The copper site displays an edge-sharing contact to adjacent Cu centers to produce {Cu₂O₂} rhombi with alternating shortlong Cu–O distances, which are connected, in turn, to form the layer structure through the {Cu₂RPO₃}₂ rings. The tau-descriptor (τ_5) value for the Cu1 atom is 0.08, which indicates no significant distortion of the geometry ($\tau_5 = 0$ for an ideal square pyramid and $\tau_5 = 1$ for an ideal trigonal bipyramid).^[8] As can be seen in Scheme 1, the fully deprotonated 2,6-naphthalenedi-



Figure 2. Cu^{II} coordination environment in 1. Symmetry codes: (i) 2 - x, -y, 2 - z; (ii) 1 - x, -1/2 + y, 3/2 - z; (iii) x, -1/2 - y, -1/2 + z; (iv) 1 - x, -y, 1 - z; (v) x, 1/2 - y, -1/2 + z; (vi) 1 - x, 1/2 + y, 3/2 - z; (vii) x, -1/2 - y, 1/2 + z; (viii) 1 + x, -1/2 - y, 1/2 + z; (vii) 2 - x, 1/2 + y, 3/2 - z; (x) 1 + x, y, 1 + z.



Figure 3. Perspective view of the 3-D framework of 1.







Scheme 3. The binding modes of NDPA-H₄ observed in this study.

phosphonate ligand adopts a μ_8 - η^2 : η^2 : η^1 : η^1 : η^1 : η^1 : η^1 coordination mode by linking Cu^{II} ions in the construction of the 3-D framework (Figure 2).

Organoimine ligands exhibit intrinsic affinity for copper centers,^[9] which can be introduced to provide square planar {Cu(terpy)}²⁺ subunits with only two available sites, one at the basal plane and one at the apical position for organophosphonate coordination. Limiting phosphonate coordination constrains structural diversity resulting in more predictable structures. The introduction of terpyridine at the copper coordination sphere provided the crystal structure of [{Cu(terpy)}(2,6-NDPA-H₃)]- $[{Cu(terpy)}(2,6-NDPA-H_3)(2,6-NDPA-H_2)]\cdot 3H_2O$ (2) where anionic complex of [Cu(terpy)(2,6 NDPA-H₃)(2,6-NDPA-H₂)]⁻ (Figure 4, a) and cationic complex [Cu(terpy)(2,6-NDPA-H₃)]⁺ (Figure 4, b) cocrystallized to provide charge balance. It is noteworthy that the crystal packing includes the anionic molecular precursor of the 1-D chain together in the same crystal structure. The 1-D cationic chain exhibits a zigzag pattern previously observed in {Cu(terpy)}²⁺-organodiphosphonate molecules.^[10] Within the cationic chains, the 2,6-NDPA-H₃ ligand adopts μ_2 - η^1 : η^1 coordination mode in binding the Cu^{II} ions in the construction of the one-dimensional chain (Figure 5). As for the geometry of Cu atom in 1, the tau-descriptor (τ_5) values for the Cu1 and Cu2 atoms in 2 are 0.04 and 0.06, respectively, indicating no significant geometric distortion.

The 2-D material **3** (Figure 6, a) and its interpenetrated hydrate **4** (Figure 7, a) were obtained under hydrothermal conditions at 120 °C and 200 °C, respectively. Both molecules can be described as possessing the zigzagged chain motif observed in **2** linked into two-dimensions (parts b of Figures 6 and 7) via VO_2^{+1} coordination at the deprotonated sites of 2,6-NDPA-H₄ to form the wavelike layers. Non-interpenetrated isomer **3** formed at low temperature (120 °C) whereas interpenetrated isomer **4** formed in increased yields with increased temperature. Above 120 °C isomer **3** disappeared and **4** was observed as the only crystalline phase at 200 °C. Both isomers form 2-D layers with the wavelike patterns shown in Figures 6c and 7c. The major difference between the two isomers is that compound **4** is an



Figure 4. The crystal structure of **2** showing (a) anionic and (b) cationic complexes. Symmetry codes: (i) 1 - x, 1/2 + y, 2 - z; (ii) 1 - x, -1/2 + y, 2 - z.



Figure 5. Perspective view of the one-dimensional complex cationic chain of ${\bf 2}$ in the *bc* plane.

interpenetrated 2-D network whereas **3** is not, as seen in Figures 6d and 7d. The angle between zigzag 2,6-NDPA-H₄ units







Figure 6. (a) Coordination environment of Cu^{II} and V^V atoms in **3**. The water molecules of crystallization are omitted for clarity. Symmetry codes: (i) -x + 1, -y, -z + 1; (ii) x + 1/2, -y + 1/2, -z + 1; (iii) x - 1/2, -y + 1/2, -z + 1. (b) The 2-D structure of **3** viewed along *ab* plane. (c) The perspective view of the pillared layer of **3** viewed along *ac* plane. (d) Topological representation of the 2-D network in **3**.

in **3** is about 17.2 ° but expands to approximately 40 ° as a result of the interpenetration in **4**. Isomer **3** exhibits wavelike layers with acute angles at the {Cu(terpy)}²⁺ corners. The taudescriptor (τ_5) values for Cu atoms in complex **3** and **4** are 0.02 and 0.21, respectively, showing that the Cu atom in **4** is more distorted than that of **3**. The VO₂⁺ tetrahedra are exclusively coordinated to the 2,6-NDPA-H³⁻ units in generating the 2-D connectivity. VO₂ tetrahedra and {Cu(terpy)}²⁺ corners are exclusively coordinated to the 2,6-NDPA-H³⁻ units. The same connectivity pattern is seen in both isomers but with different bond angles and lengths. A list of selected bond lengths and angles for complexes **1–4** are provided in Table S2–S5 (Supporting Information). Isolated VO₂ tetrahedra have been previously observed in three dimensional Cu–V–P–O molecules.^[11] Structural



Figure 7. (a) Coordination environment of Cu^{II} and V^V atoms in **4**. Symmetry codes: (i) x + 3/2, -y + 1/2, z + 1/2; (ii) x + 1/2, -y + 1/2, z - 1/2; (iii) x - 3/2, -y + 1/2, z - 1/2; (iv) x - 1/2, -y + 1/2, z + 1/2. (b) The perspective view of the single layer **2** viewed along ac plane. (c) The perspective view of the pillared layer of **4**. (d) The perspective view of parallel 2-D \rightarrow 2-D interpenetration of two neighbouring sheets colored in green and red.

characteristics of 2-D and 3-D V–P–O molecules are given in Table S6 (Supporting Information).

To better understand the structure of isomers **3** and **4**, topological analysis^[12] was employed to describe these architectures. Complex **3** features a three-connected **hcb** Shubnikov hexagonal plane net with 6³ topology. On the other hand, the network of compound **4** displays a parallel twofold $2\text{-D} \rightarrow 2\text{-D}$ interpenetration, upon considering 2,6-NDPA-H₄ ligand as 4-connected nodes, and Cu and V atoms as 2-connected nodes, respectively (parts d of Figures 6 and Figure 7).

The thermal behavior of 1, 2, 3, and 4 was studied by TGA. Thermogravimetric analysis of crystalline 1 shows two steps of decomposition. The first weight loss of about 8.8 % is attributed to the Cu^{II}-coordinated water molecule (8.0 % calculated); the second approximately 22.8 % weight loss at about 400 °C corresponds to decomposition of the 2,6-NDPA (26.8 % calculated) Figure S1 (Supporting Information). Both terpy and 2,6-NDPA units decompose concurrently in sample 2 with a total weight loss of approximately 47.8 % (56.8 % calculated), Figure S2 (Supporting Information). Thermogravimetric analysis of crystalline 3 and 4 revealed that 3 starts to decompose at about 210 °C while the interpenetrated isomer 4 is thermally stable to about 300 °C as seen in Figures S3 and S4 (Supporting Information). The weight loss before 400 °C can be ascribed to the decomposition of the organoimine ligands whereas Cu/V-organophosphonate decomposition usually starts at about 400 °C and above. The onset of decomposition of organoimine groups at 210 °C in **3** is associated with the non-interpenetrated packing of the two-dimensional network whereas interpenetrated isomer **4** has a higher density with the organoimine units, which are well embedded in the structure. Sample 3 shows 16.4 % weight loss until 300 °C and 4 shows an 18.4 % weight loss in two sharp curves, which could be attributed to the presence of interpenetrated two-dimensional networks. TGA analysis of 3 exhibits two distinct steps for organoimine and organophos-

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phonate decompositions with a total weight loss of 52.5 % of the organic units (52.2 % calculated) whereas TGA analysis of **4** reveals a total weight loss of 47.7 % for the organic units (49.3 % calculated, Figure S4, Supporting Information). The TGA curve of **3** shows that a 31.6 % weight loss occurs in two steps corresponding to the decomposition of terpy units (33 % calculated). The final approximately 20.9 % pattern of weight loss is attributed to the organic components of 2,6-NDPA-H₄ (calculated 14.9 %).

Both samples show weak ferromagnetic ordering at room temperature as seen in Figure 8. The insets in Figure 8 illustrate the mechanically separated and purified crystals of 3 and 4 used in the magnetic studies. Prior to the magnetic analysis, the crystals larger than 200 µm were hand-picked under the microscope and washed with water and acetone on a fritted pyrex filter (40-100 µm) to remove any unseen impurities. Magnetization was measured with a vibrating sample magnetometer in a Quantum Design PPMS system. The offsets in the magnetization measurements indicate that a magnetic moment is present in the sample as opposed to simple paramagnetic behaviour (which typically appears as a straight line passing through the origin). This magnetic moment is very small but is, in fact, measurable. The extra magnetization is the offset in the magnetization axis shown by the guidelines to the slope of the magnetization curve at high fields, which is 0.06 emu/g for 3 and 0.02 emu/g for 4. Although the molecule was washed intensely with water and acetone prior to the magnetic analysis, the weak signal at room temperature may still be attributable



Figure 8. Magnetization measurements of (a) ${\bf 3}$ and (b) ${\bf 4}$ showing ferromagnetic behaviour at 300 K.

to vanadium oxide trace impurities.^[13] Notably, it still is not easy to correlate impurities as the sources of magnetism in bimetallic systems. Further experiments, such as neutron diffraction studies, are required to more fully understand the sources of magnetism in **3** and **4**.

Conclusions

We synthesized a structurally rigid novel 2,6-naphthalenediphosphonic acid linker and a series of novel hybrid frameworks of the Cu-organophosphonate family incorporating this ligand. We further modified the Cu^{II} coordination sphere with terpy. Constraining the copper coordination sphere to produce the square pyramidal {Cu(terpy)}²⁺ building unit was instrumental to generating anionic molecular **2a** and the cationic zigzagged one-dimensional chain of 2c. The evolution of the one-dimensional chain structure from its molecular precursor resulted in encapsulation in the same structure of 2. Furthermore, site specific coordination of the VO₂⁺¹ subunit at the deprotonated sites of 2,6-NDPA-H₂ expanded the 1-D chains in the crystal structure of 2c to form the 2-D wavelike layers of 3 and its interpenetrated hydrate 4. Increasing the reaction temperature provided bond flexibility enabling the layers in 3 to expand to allow interpenetration in 4. Starting with "naked" copper coordination, three-dimensional compound 1 was prepared via the coordination of four deprotonated oxygens arms of the phosphonate to four available coordination sites on Cu^{II}, where the fifth coordination site is occupied by a water molecule. Unlike previous examples with aliphatic diphosphonates, structurally rigid aromatic 2,6-NDPA-H₄ retains structural integrity thus giving rise to predictable higher dimension structures. Engineering the copper coordination sphere with organoimine ligands has proven to be a promising method for transitioning ambiguous two and three-dimensional structures into predictable and tunable functional materials.

Experimental Section

Reagents and General Procedures: All reagents were purchased from Aldrich, Merck and Alfa Aesar and used as received without any purification. The syntheses of complexes **1–4** were carried out in 23 mL polytetrafluoroethylene-lined stainless steel containers under autogenous pressure. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument.

Synthesis of 2,6-naphthalenediphosphonic acid (2,6-NDPA-H₄): Naphthalene-2,6-diyl-bis(phosphonic diisopropyl ester) was obtained using a $[Pd(PPh_3)_4]$ -catalyzed Michaelis–Arbuzov reaction by conventional heating methods. A mixture of 2,6-dibromonaphthalene (1.0 g, 3.5 mmol), triisopropylphosphite (13.5 mL, 55 mmol) and $[Pd(PPh_3)_4]$ (38 mg, 0.016 mmol) was added in a 50 mL flask and heated to 200 °C under argon atmosphere (14 mL/min). After 1 h, reflux was started and the temperature was kept at 200 °C for 4 h. With the temperature constant at 200 °C, triisopropylphosphite (4.0 mL, 16.2 mmol) and $[Pd(PPh_3)_4]$ (38 mg, 0.016 mmol) were added to the reaction flask as a second addition. After this addition, the temperature was increased to 220 °C and reaction was continued for 20 h. Upon fast cooling in a refrigerator, the white crystalline solid product was precipitated and filtered with a Gooch filter by





washing with *n*-hexane (yield; 1.44 g, 91 %). Spectral data: ¹H NMR (500 MHz, CDCl₃): $\delta = 8.47$ (d, J = 15.3 Hz, 5 H), 8.00 (dd, J = 8.4, 3.9 Hz, 5 H), 7.89–7.80 (m, 5 H), 7.27 (s, 2 H), 4.99–4.62 (m, 12 H), 1.76 (s, 6 H) ppm. 1.15 g Naphthalene-2,6-diylbis(phosphonic diisopropyl ester) (2.5 mmol) and 20 mL of HCl (37 %) were added in a 50 mL flask and heated to 80 °C on a sand bath to synthesize naphthalene-2,6-diylbis(phosphonic acid). After 8 h, a white, pastelike mixture was obtained and this mixture was treated with methanol to remove excess hydrochloric acid and isopropylchloride which is generated during acid-catalyzed hydrolysis. This methanol-crude product mixture was obtained as a white solid (yield; 720 mg, 99 %). Spectral data: ¹H NMR (500 MHz, CDCl₃): $\delta = 7.49$ (s, 4 H), 7.31 (d, J = 19.1 Hz, 2 H), 7.25 (s, 6 H), 1.43 (s, 5 H) ppm.

Synthesis of [{Cu(H₂O)}(NDPA)_{0.5}] (1): A mixture of CuSO₄-5H₂O (0.129 g, 0.52 mmol), naphthalene-2,6-diylbis(phosphonic acid) (0.100 g, 0.35 mmol), and water (10.084 g, 560 mmol) were stirred gently and heated to 180 °C in a 23 mL polytetrafluoroethylene lined stainless steel container under autogenous pressure for 72 h. The pH of the mixture was adjusted to 2 by adding 10 % HNO₃ After the reaction, the vessel was cooled to room temperature slowly and precipitate was filtered out by washing with distilled water and acetone. Light green, rectangular plates were obtained with 10 % yield. Compound 1 starts to decompose at about 400 °C and decomposition continues until approximately 850 °C. $C_5H_5CuO_4P$ (223,61): calcd. C 26.86, H 2.25; found C 26.76, H 2.31.

[{Cu(terpy)}(2,6-NDPA-H₃)][{Cu(terpy)}(2,6-NDPA-H₃)(2,6-NDPA-H₂)]-3H₂O (2): A mixture of CuSO₄·5H₂O (0.129 g, 0.52 mmol), 2,2' :6',2''-terpyridine (0.072 g, 0.31 mmol), naphthalene-2,6-diyl-bis(phosphonic acid) (0.100 g, 0.35 mmol), and water (10.084 g, 560 mmol) were stirred gently and heated to 120 °C in a 23 mL polytetrafluoroethylene lined stainless steel container under autogenous pressure for 24 h. The pH of the mixture was adjusted to 1.5 by adding 10 % HNO₃. After the reaction, the vessel was cooled to room temperature slowly and precipitate was filtered out by washing with distilled water and acetone. Blue block crystals were obtained with a small amount of white and green powdery phases. Compound **2** starts to decompose at about 375 °C and the decomposition continues above 850 °C. $C_{60}H_{54}Cu_2N_6O_{21}P_6$ (1508.03):

calcd. C 47.79, H 3.61, N 5.57; found C 47.59, H 3.52, N 5.52.

[{Cu(terpy)}VO₂(2,6-NDPA-H)] (3): A mixture of CuSO₄·5H₂O (0.129 g, 0.52 mmol), Na₃VO₄ (0.060 g, 0.33 mmol), 2,2':6',2''-terpyridine (72 mg, 0.31 mmol), naphthalene-2,6-diylbis(phosphonic acid) (100 mg, 0.35 mmol), HF (one drop to adjust the pH to 1.5) and water (10.084 g, 560 mmol) were stirred gently and heated to 120 °C in a 23 mL polytetrafluoroethylene lined stainless steel container under autogenous pressure for 48 h. After the reaction, the vessel was cooled to room temperature slowly and precipitate was filtered out by washing with distilled water and acetone. Blue rectangular plate crystals were obtained with a small amount of powder phase. Compound **3** starts to decompose around 400 °C and the decomposition continues above 650 °C. $C_{25}H_{20}CuN_3O_9P_2V$ (682.875): calcd. C 43.97, H 2.95, N 6.15; found C 43.91, H 2.88, N 6.09.

 $\label{eq:contemp} $$ VO_2(2,6-NDPA-H)]-H_2O$ (4): A mixture of CuSO_4-5H_2O$ (0.129 g, 0.52 mmol), Na_3VO_4$ (0.060 g, 0.33 mmol), 2,2':6',2''-terpyridine (0.072 g, 0.31 mmol), naphthalene-2,6-diylbis(phosphonic acid) (0.100 g, 0.35 mmol), HF (one drop to adjust the pH to 1.5) and water (10.01 g, 560 mmol) were stirred gently and heated to 200 °C in a 23 mL polytetrafluoroethylene lined stainless steel container$

under autogenous pressure for 48 h. After the reaction, the vessel was cooled to room temperature slowly and the resulting precipitate was filtered out by washing with distilled water and acetone. Green rectangular plate crystals were obtained with a small amount of powder phase. Compound **4** starts to decompose at around 400 °C and the decomposition continues above 650 °C. $C_{25}H_{18}CuN_3O_8P_2V$ (664.86): calcd. C 45.16, H 2.73, N 6.32; found C 45.25, H 2.71, N 6.35.

X-ray Data Collection and Structure Refinement Details

X-ray Data Collection and Structure Refinement Details for Complexes 1 and 2: Data for complexes 1 and 2 were obtained with two different diffractometers, Bruker Apex II CCD and Bruker Apex II QUAZAR. Indexing was performed using APEX2.^[S1] Data integration and reduction were carried out with SAINT.^[S2] Absorption correction was performed by multi-scan method implemented in SADABS.^[S3] The Bruker SHELXTL^[S4] software package was used for structure solution and structure refinement. All non-hydrogen atoms were refined anisotropically using all reflections with $l > 2\sigma(l)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. In complex 1, the H atoms (H1w and H2w) of water molecule were located in a difference Fourier map and the O-H distances restrained to be 0.84 Å from O atom using DFIX command and their positions were constrained to refine on their parent O atoms with $U_{iso}(H) = 1.5Ueq(O)$. In complex 2, the water oxygen atom is disordered over two sites (O21 and O22) with occupancies of 0.31:0.69, and the H atoms of disordered water molecule could not be located from the difference Fourier map. The other H atoms (H9O, H10O, H11O and H12O) in water molecules of complex 2 were placed at calculated positions using WinGX program.^[S5] The hydroxyl groups (-P-OH) in 2 were found in the difference Fourier map and refined using a riding model. Crystal structure validations and geometrical calculations were performed using Platon software.^[S6] Mercury software^[S7] was used for visualization of the cif file.

X-ray Data Collection and Structure Refinement Details for Complexes 3 and 4

Suitable single crystals of complexes **3** and **4** were selected under a microscope with polarized light and data sets were collected on a Bruker SMART Platform diffractometer equipped with an Apex-I detector. The crystals were kept at 100.0 K during data collection. Using Olex2^[S8] the structures were solved with the Superflip^[S9–S11] structure solution program using Charge Flipping and refined with the ShelXL^[S12] refinement program using Least Squares minimization. Crystallographic details for the structures of **3** and **4** are summarized in Table S1 (Supporting Information). The interpenetrated isomer is disordered with exception of V1, O1 and O2, all remaining atoms are disordered with a major component of 93 % and a minor component of 7 %. All crystals from this batch showed the same behavior.

CCDC 1058349 (for 1), 1431497 (for 2), 1400476 (for 3), and 1062838 (for 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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