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Pyro without Fire: Synthesis, Structure, and Reactivity of a Dimeric Vanadyl Pyrophosphate Coordination Complex

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Supporting Information

ABSTRACT: The complex $\{[(V^{IV}O)bipy(H_2O)]_2(\mu\text{-}P_2O_7)\}\cdot 3H_2O$ (**2**) was readily obtained as a nanocrystalline powder by one-pot synthesis under mild conditions. Single crystals of **2** were grown at room temperature over 2 months, and its structure was determined. Fundamental catalytic activity was proven for this species by testing for oxidation of benzyl alcohol in air.

Over the last 4 decades, there has been considerable interest in the vanadium−phosphorus oxide (VPO)-catalyzed oxidation of butane to maleic anhydride.[1,2] Industrial VPO catalysts typically consist of vanadyl phosphate polymeric precursors that in situ and at relatively high temperatures (>700 K) transform into vanadyl pyrophosphate $[(V^{IV}O)_2P_2O_7$ (VPP)], a process that remains currently under investigation.[1,2] In an effort to develop a homogeneous system to bypass such complexity, some years ago Herron et al. from DuPont succeeded in the preparation of a soluble, nonpolymeric precursor to VPP, the cyclic tetramer $(A)_4[(V^{IV}O)_4(\mu\text{-}OCH_3)_4(\mu\text{-}P_2O_7)_2]$ [**1a**; A = protonated 1,8-bis-(dimethylamino)naphthalene].[3] Although the success of this study was limited in terms of catalytic activity/selectivity, the work demonstrated for the first time the possibilities of producing vanadium pyrophosphate (V-PPi) "cores" directly, i.e. not as result of phosphate condensation under extreme reaction conditions. A similar anionic cyclic assembly with formula $Li_8[V^{IV}OP_2O_7(H_2O)\cdot 4H_2O]_4$ (**1b**) was more recently reported by the Cummins group.[4] Yet, native **1a** or **1b** has not been catalytically tested so far. Moreover, as far as we know, no other discrete V-PPi species has been documented in the literature whose synthesis was carried out in mild conditions.

In recent years, we have reported a wealth of PPi molecular complexes with a variety of intriguing chemical−physical and/or biological properties.[5] Encouraged by successful outcomes with other first-row transition metals[5b−h] and inspired by the VPO catalytic process, we have been pursuing the synthesis of a V-PPi complex, although the structures of such molecular assemblies proved elusive.

The isolation of a possible $V^{IV}O$-PPi species,[5h] obtained in high yield as an insoluble lime-green powder via a one-pot synthesis at room temperature (RT) by the reaction of $V^{IV}OSO_4$ with 2,2′-bipyridine (bipy) and $Na_4P_2O_7$ in water, was reported previously by one of us (R.P.D.). After multiple attempts to crystallize this putative species using a variety of starting vanadium salts and solvents, light-green crystals suitable for X-ray diffraction were obtained during the course of this study by slow diffusion methods at RT (experimental details are given in the Supporting Information, SI; note no hydrolysis of PPi was observed throughout).

Herein, we disclose the structure and characterization of a novel, noncyclic VPP complex, $\{[(V^{IV}O)bipy(H_2O)]_2(\mu\text{-}P_2O_7)\}\cdot 3H_2O$ (**2**), offering up a discrete V-PPi core with cis arrangement of the vanadyl units in a facile and high-yielding reaction in mild conditions. Fundamental reactivity studies conducted with **2** show catalytic activity, although each metal ion in the starting complex is coordinatively saturated. The catalytic aerobic oxidation of benzyl alcohol (ba) was used as a benchmark reaction because this would allow for facile product identification and a comparison of the reactivity of **2** with previously reported vanadium catalysts.[6] Initial data suggest that the PPi core of **2** remains intact in solution, highlighting the possibility of VPP species as the paradigm to shift from purely solid-state "VPO" approaches to molecular-type "V-PPi" catalysis, at least for selected substrates.

Single-crystal X-ray diffraction analysis revealed that **2** crystallizes in the monoclinic space group *C*2/*c* with a half-molecule in the asymmetric unit, with the second half being generated by the crystallographic inversion center. Each metal center in **2** is six-coordinated, in a distorted octahedral geometry, with the N(1)−V═O fragment identifying the axial direction, a water molecule in an equatorial site completing the metal coordination sphere, and the PPi ligand adopting a common[7] bis-bidentate coordination mode (Figure 1a). The two V═O units are syn-oriented, and in contrast to that noted in **1a** and **1b**,[3,4] they align toward each other, with the O···O distance [3.208(3) Å] being much shorter than the intradimer V···V separation [4.4856(8) Å]. Additionally, in **2**, the two V═O bonds are aligned in the opposite direction with respect to the PPi bridge (Scheme S1 in the SI), as reflected in both the V═O···O═V distance [about 6.7−7.5 Å for **1a** and **1b** vs 3.2 Å for **2**] and the V═O···O═V torsion angle [in the range 0−5.6° for **1a** and **1b** vs 30° for **2**]. The extensive network of hydrogen bonds in **2** likely stabilizes this unusual

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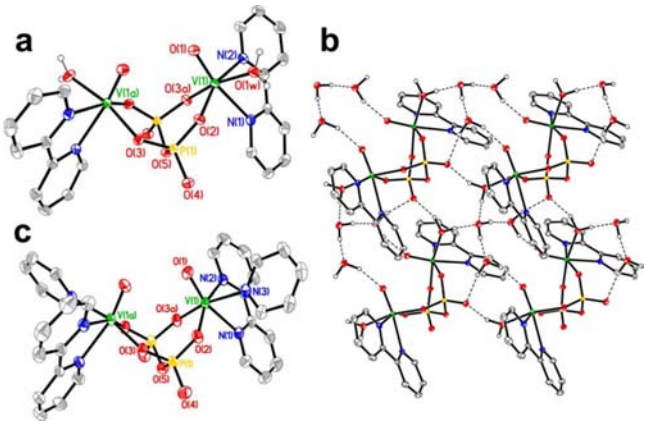

Figure 1. Molecular structure of the V-PPi dimeric unit in **2** (a) and **2-pyr** (c) (ellipsoids at the 50% probability level), with atom-labeling scheme [a: $-x + 2$, y, $-z + {}^{3}/_{2}$]. Selected bond lengths (Å) for **2**: V(1)−O(1) 1.608(2), V(1)−O(2) 1.966(2), V(1)−O(3a) 1.966(2), V(1)−O(1w) 2.038(2), V(1)−N(1) 2.286(2), V(1)−N(2) 2.146(2). Selected bond lengths (Å) for **2-pyr**: V(1)−O(1) 1.604(1), V(1)−O(2) 1.947(1), V(1)−O(3a) 1.976(1), V(1)−N(1) 2.291(1), V(1)−N(2) 2.144(1), V(1)−N(3) 2.165(1). (b) Projection along the *c* axis of the supramolecular 2D layer in **2**. H atoms on the bipy and pyr ligands are omitted for clarity.

arrangement, with the interactions between the crystallization water molecules and the two V═O units resulting in the formation of a stable closed-ring motif. Hydrogen-bonded dimeric units organize into supramolecular layers extending parallel to the *ab* plane, where the formation of several such hydrogen-bonding ring motifs can be observed (Figure 1b). These layers are then stacked along the crystallographic *c* axis by means of $\pi-\pi$ interactions between bipy ligands on neighboring molecules (Figure S8 in the SI).

The presence of aromatic stacking, coupled with the robustness of the hydrogen-bonding network, most likely accounts for the lack of solubility noted for **2**. Notably, a possibly partially dehydrated, amorphous phase of **2** (**2-anhydr**), with a water content varying from 1 to 2 retained molecles per dimeric unit, could only be obtained by heating the sample at 200 °C for several hours.[8]

Fundamental catalytic tests were conducted in neat ba at 100 °C under reflux, using samples of **2** rapidly obtained by direct synthesis and duly characterized.[8] The percent conversion of ba to benzaldehyde was determined from ^{1}H NMR analysis after 72 h. The results are collected in Table 1. In the absence of additives/promoters, the conversion detected was not satisfactory. The addition of triethylamine (NEt_3),[6] however, led to a significant improvement of the reactivity of **2**. For instance, oxidation of ba with only 0.1 mol % **2** in the presence of 10 mol % NEt_3 afforded benzaldehyde in 34% yield after 72 h at 100 °C. Over longer reaction times (5−6 days) and under the same reaction conditions (neat ba, 10 mol % NEt_3), quantitative conversion was observed with 1 mol % **2**, yielding a mixture of benzaldehyde (∼10%) and benzoic acid (∼90%). The addition of 20 mol % NEt_3 further enhanced the catalytic activity of **2**, affording benzaldehyde in 66, 80, or 100% (with no benzoic acid) yield for catalyst loads of 0.1, 0.5, or 1 mol %, respectively.

During the course of a typical reaction in the presence of NEt_3, dissolution of **2** was observed within the initial 1−4 h, with a green precipitate noted in the reaction flask within 24 h (Figure 2a). This homogeneous−heterogeneous path was

Table 1. Aerobic Oxidation of ba Catalyzed by 2[a]

entry	mol % **2**	atm	additive (mol %)	% conversion
1	1	air	none (10)	8 ± 2
2	1	air	pyr (10)	16 ± 4
3	1	air	Et_3N (10)	36 ± 3
4	0.5	air	Et_3N (10)	31 ± 5
5	0.25	air	Et_3N (10)	31 ± 3
6	0.1	air	Et_3N (10)	34 ± 2
7	2	air	Et_3N (10)	54 ± 4
8	5	air	Et_3N (10)	54 ± 7
9	1 (DMSO)	air	Et_3N (10)	60 ± 2
10	1 (toluene)	air	Et_3N (10)	21 ± 1
11	1	air	Et_3N (20)	100
12	0.5	air	Et_3N (20)	80 ± 4
13	0.1	air	Et_3N (20)	66 ± 1

[a]Reaction conditions, unless otherwise stated: 1 mL of substrate, no solvent (neat), 100 °C, 72 h.

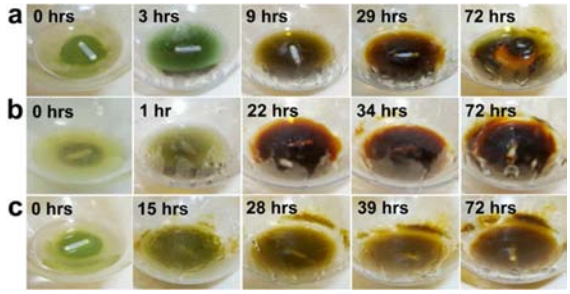

Figure 2. Snapshots of the ba oxidation reaction at various time points (selected examples): (a) ba + 10 mol % NEt_3 + 1 mol % **2** in air at 100 °C; (b) ba + 20 mol % NEt_3 + 1 mol % **2** in air at 100 °C; (c) ba + 10 mol % pyr + 1 mol % **2** in air at 100 °C.

accompanied by a chromatic evolution of the reaction solution from green (homogeneous phase) to dark orange (heterogeneous phase), as shown in Figure S10 in the SI.

To investigate the nature of the active catalytic species, the reaction mixture was tentatively analyzed by ^{31}P and ^{51}V NMR, as well as mass spectrometry.[8,9] In the decoupled ^{1}H{^{31}P} NMR spectrum of the reaction mixture, a signal centered around 3 ppm was observed after 72 h, consistent with a coordinated PPi moiety.[5a] The same signal was observed during the initial homogeneous phase (green solution), as well as in the spectrum of **2-anydr** (Figure S5 in the SI). A MALDI-ToF analysis of the reaction mixture after 72 h resulted in the detection of several peaks, some of which were consistent with the existence in solution of monovalent (V^{IV}) or mixed-valent (V^{IV}/V^{V}) PPi-bridged species (Figures S16−S18 in the SI). Bands corresponding to the presence of coordinated bipy appeared in the IR spectrum of the dark-green precipitate recovered after 72 h, together with a broad band in the range 1000−1100 cm^{-1}, which is indicative of coordinated PPi.[8]

Overall, the data suggest that coordination of ba[10a] to the V-PPi core may occur in solution while the V-PPi core remains intact and that one or multiple charged species may form, as is also suggested by the improved reactivity in polar versus nonpolar solvents (entries 9 and 10 in Table 1).

In an attempt to clarify the role of the base in the catalytic mechanism, we also investigated the reaction of ba oxidation using **2** with added pyridine (pyr).[10] In this case, **2** did not dissolve (Figure 2b) and a yellow-brownish crystalline precipitate was recovered after 72 h. Single-crystal X-ray

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diffraction indicated that pyr coordination to the V-PPi core had occurred, affording $\{[(VO)bipy(pyr)]_2(P_2O_7)\}$ (**2-pyr**; Figure 1c). **2-pyr** is structurally very similar to **2**, the main difference being that the pyr molecule in **2-pyr** replaces the equatorial water molecule of **2**. Lower activity was noted in the presence of pyr compared to NEt_3, suggesting that coordination of the base to the vanadium center does not promote catalyst turnover, as is observed for some homogeneous vanadium catalysts.[10a−c] Sanford et al. recently demonstrated that the addition of pyr could serve to either promote catalysis (as was initially predicted to happen for **2**) or impede it because of metal coordination site saturation, in a concentration-dependent manner.[10d] Preliminary results using **2-anhydr** as the catalyst revealed improved activity with respect to **2** (with 70−80% conversion observed, on average, with 1 mol % **2-anhydr** and 10 mol % NEt_3 at 100 °C for 72 h), also supporting the idea of the free equatorial coordination site being fundamental for catalysis. This point will be further investigated in future mechanistic work.

In summary, the initial results that we report herein offer a rare V-PPi coordination complex with confirmed catalytic activity under relatively mild conditions possibly proceeding through an intriguing homogeneous−heterogeneous catalytic route. We believe this approach offers significant potential as a platform for future investigations, including fundamental catalytic mechanistic studies and rational catalyst design for mild oxidations through V-PPi "cores". This work prospects a potential paradigm shift for the VPO field, focusing on a discrete molecular entity, expanding the perspective from purely solid-state to coordination chemistry. The two new structures presented herein are valuable additions to the current array of metal pyrophosphate coordination complexes and demonstrate that mild vanadium phosphate chemistry is indeed possible. The synthesis of further such examples as well as the study of the reactivity of **2** toward a variety of substrates is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthetic procedures, and crystallographic and catalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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