Single Crystal-to-Single Crystal Irreversible Transformation from a Discrete Vanadium(V)−Alcoholate to an Aldehydic-Vanadium(IV) Oligomer

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Abstract: An unprecedented single crystal-to-single crystal transformation occurs when a binuclear oxovanadium(V) compound $[V^V_2O_2(L)_2]$ **1** involving 2,6-bis(hydroxymethyl)-*p*-cresol (H_3L) as a bridging ligand is exposed simultaneously to white light and aerial oxygen to generate an oligomeric compound $[V^{IV}_2O_2(L^*)_2]$ **2** (H_2L^* is 3-hydroxymethyl-5-methylsalicylaldehyde). Each vanadium(V) center in **1** is reduced to vanadium(IV) in **2** at the expense of a two-electron alcohol-to-aldehyde oxidation in the coordinated ligand. The additional electron being released is possibly consumed by molecular oxygen to generate hydrogen peroxide.

Single crystal-to-single crystal (SCSC) transformations involve coordinated movement of atoms in the solid matrices. Most of these transformations are reversible in nature and are triggered by light,[1] albeit a few thermally induced incidences are also known.[2] A good number of these studies have been reported for organic molecules,[1a,c−f] while crystals of metallo−organic frameworks usually fail to retain their crystallinity after the generally robust rearrangements that occur in the solid phase. Nevertheless, quite a few SCSC transformations involving coordination compounds have been reported in recent years[1b,2a,c,e,3] that are accompanied by many interesting changes in properties such as host−guest behavior,[3a−c] magnetism,[2e,3d] and photochemical reactivity.[3e] Herein, we report a binuclear oxovanadium(V) compound $[V^V_2O_2(L)_2]$ **1** involving 2,6-bis(hydroxymethyl)-*p*-cresol (H_3L) as a bridging ligand, which on exposure to white light in air, undergoes an unprecedented coordination-driven oligomerization in the solid state to an infinite one-dimensional (1D) chain of oxovanadium(IV) entity $[V^{IV}_2O_2(L^*)_2]_\infty$ **2** in 100% yield through a SCSC transformation that ends up with a redox process leading to the reduction of the metal centers with concomitant oxidation of the organic component. We have investigated this transformation by X-ray diffraction, IR and UV−vis spectroscopy, magnetic susceptibility measurements, and EPR spectroscopy.

The interest in the coordination chemistry of H_3L as ligand has been invigorated in recent years because of the variable modes (μ_2 or μ_3) of coordination provided by this oxido-rich molecule, leading to the isolation of organic−inorganic hybrid architectures with multiple metal centers.[4] In continuation of our long-standing interest in vanadium coordination chemistry,[5] we sought to explore the chemistry of this alcohol-rich ligand with vanadium as the metal ion source. When VO(acac)$_2$ was reacted with H_3L in 1:1 molar ratio in dichloromethane, a dark-red crystalline compound **1** was obtained. X-ray diffraction analysis[6] of **1** has revealed it to be a centrosymmetric molecule with two five-coordinated vanadium(V)

centers connected by a pair of bridging phenoxido oxygen atoms, each coming from a fully deprotonated ligand ($L^{3−}$) with three units of negative charge to meet the requirement of vanadium(V) (Figure 1a). The average C−O bond distances of the alkoxides (1.419 Å) and phenoxides (1.385 Å) are in the expected range, as are the average V−O (phenoxido) (2.017 Å) and V−O (alkoxido) (1.786 Å) distances.
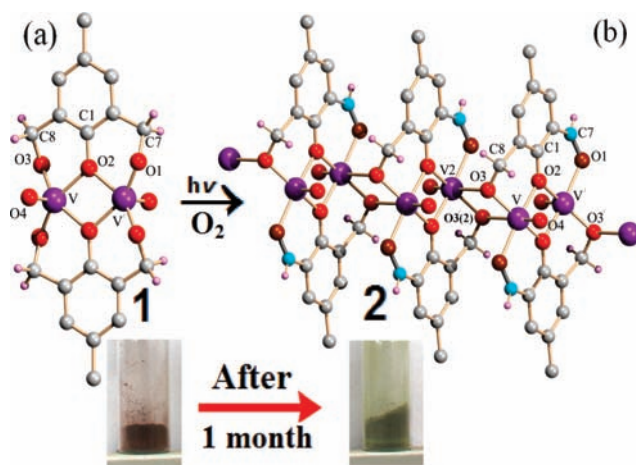

Figure 1. Perspective views of the binuclear vanadium(V)−alcoholate complex **1** (left, a) and the vanadium(IV)−aldehyde oligomer **2** (right, b).

Crystals of **1**, on being kept in the air at the ambient temperature for about a month or so, undergo an irreversible coordination-driven SCSC transformation to yield a greenish brown product **2** (the color change is shown in Figure 1 with powdered samples of **1** and **2**). Both compounds **1** and **2** are sparingly soluble in common organic solvents. Crystal structure determination for **2**[6] has revealed that an internal redox process is involved to bring about this change. In the net process, one alcoholate functionality of the ligand in **1** is oxidized to an aldehyde moiety with simultaneous reduction of the oxovanadium(V) to oxovanadium(IV) center. A perspective view of **2** (Figure 1b) reveals that, unlike its precursor, the metal centers in it are all vanadium(IV) with distorted octahedral coordination environment. A change from five- to six coordination has its influence on the displacement of the vanadium center from the basal O_4 plane that changes substantially from 0.336 to 0.257 Å in going from **1** to **2**.

Perhaps the most interesting structural feature of **2** is the manifestation of an internal redox process that appears to be the driving force behind this unique transformation. One of the coordinated alkoxido group (C7−O1) of the completely deprotonated tridented ligand $[L^{3−}]$ in **1** undergoes two-electron oxidation to an aldehydic C=O group, as reflected by the remarkable shortening of the bond length

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Table 1. Dynamics followed via Crystal Structure Monitoring

no. of day	C1−O2 / C7−O1(Å)	V−O4 / V′−O1(Å)	V−O3 / V2−O3(Å)	separation between monomer (Å)
1	1.385(3) / 1.401(4)	1.574(2) / 1.762(2)	1.8106(19) / 2.556(4)	3.368
8	1.384(4) / 1.381(5)	1.579(3) / 1.804(3)	1.829(2) / 2.492(8)	3.345
12	1.382(3) / 1.368(4)	1.584(2) / 1.819(2)	1.839(2) / 2.465(2)	3.333
14	1.348(14) / 1.305(15)	1.600(9) / 2.005(9)	1.923(8) / 2.292(9)	3.269
28	1.342(13) / 1.268(16)	1.615(9) / 2.064(9)	1.937(7) / 2.259(8)	3.256
35	1.347(14) / 1.244(18)	1.627(9) / 2.076(10)	1.936(8) / 2.250(10)	3.251

from 1.401(4) Å to 1.244(18) Å in going from **1** to **2** (Table 1). Thus, the anion of a new ligand, 3-hydroxymethyl-5-methylsalicylaldehyde (H$_2$L*), is generated in **2** during this oxidation, having two types of C−O bonds (C7−O1 1.244(18) Å and C8−O3 1.417(15) Å) attached as the side arms to the aromatic ring. The binuclear entities of both **1** and **2** have closely similar compositions, viz. [(VO)$_2$L$_2$] and [(VO)$_2$L*$_2$], respectively, with subtle differences in the oxidation states of vanadium, charges of the ligand anions L(3−) and L*(2−), and reduction of formula weights by 2 mass units. The individual monomeric units in **2** are finally connected together by the alkoxido bridge via the O3 atom which binds the two adjacent vanadium centers (V and V2 as shown in Figure 1b) of two monomeric units, forming two V−O bonds of strikingly different lengths. The axial V−O3′(2) bond (2.25(10) Å) is much longer compared to the equatorial V−O3 distance (1.936(8) Å) due to the strong trans labilizing influence of the terminal oxido- group O4. The increased terminal V=O$_t$ bond length in **2** (1.627(9) Å) compared to that in **1** (1.574(2) Å) also supports the lowering of the oxidation state of vanadium in **2** than that of **1**.[7] The axial−equatorial mode of bridging by the alkoxido oxygens (O3 and O3′) allows the individual monomeric units to stack one over the other, creating a staircase type of 1D chain structure in **2**. When viewed along the crystallographic *b*-axis, an overlaying type of structure is generated (Figure S1 in Supporting Information) where the centroids of the individual aromatic ring planes in the structure are separated by 3.251 Å, giving a clear indication of strong π−π interaction.
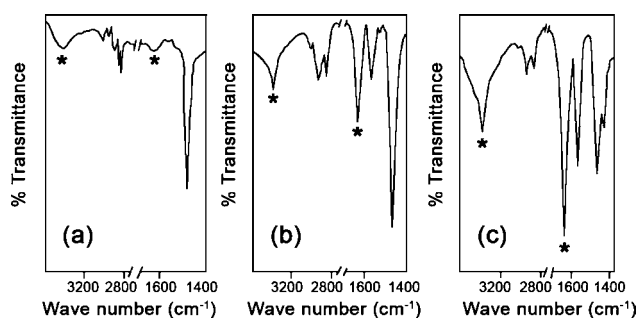

Figure 2. Time interval IR spectra of **1** recorded (a) immediately after its isolation, (b) after 10 days of exposure, and (c) after 30 days of exposure to white light, showing gradual development of two new bands (marked with asterisks) at 1625 [ν(C=O)] and 3367 [ν(aldehydic C−H)] cm^{-1}.

It is important to note that throughout this SCSC transformation of **1** to **2**, the monoclinic space group *P*2$_1$/*c* is retained, while the unit cell dimensions show only nominal changes (Table S1, Supporting Information). Clearly, this is a case of topotactic transformation where the crystallographic axes and the angles of the reactant (**1**) and product (**2**) molecules remain almost unchanged.[8] Although SCSC reactions are usually homogeneous, the present transformation appears to be heterogeneous in nature proceeding inward from the surface of the crystal. The rate of the reaction is faster when the sample is in powdered form compared to that in the crystalline state.

The progress of the formation of **2** from **1** when followed by IR spectroscopy provides corroborative evidence in support of the involvement of an internal redox process. Thus, the formation of carbonyl functionality from alcohol is apparent from the growth of a sharp new band at 1625 cm^{-1} (Figure 2) when a freshly prepared sample of **1** is subjected to time interval IR scan. In addition, another new band at 3367 cm^{-1} is generated simultaneously, as could be expected for the aldehydic C−H stretch. Further, a sharp signature band at 978 cm^{-1} due to terminal V=O$_t$ stretch in **1** is shifted to lower wavenumber at 960 cm^{-1} (not shown in Figure 2), providing evidence in support of a concomitant change in vanadium oxidation state and/or coordination geometry around the metal centers in **2**.

Scheme 1. Proposed Mechanistic Pathway for the Single Crystal-to-Single Crystal Transformation
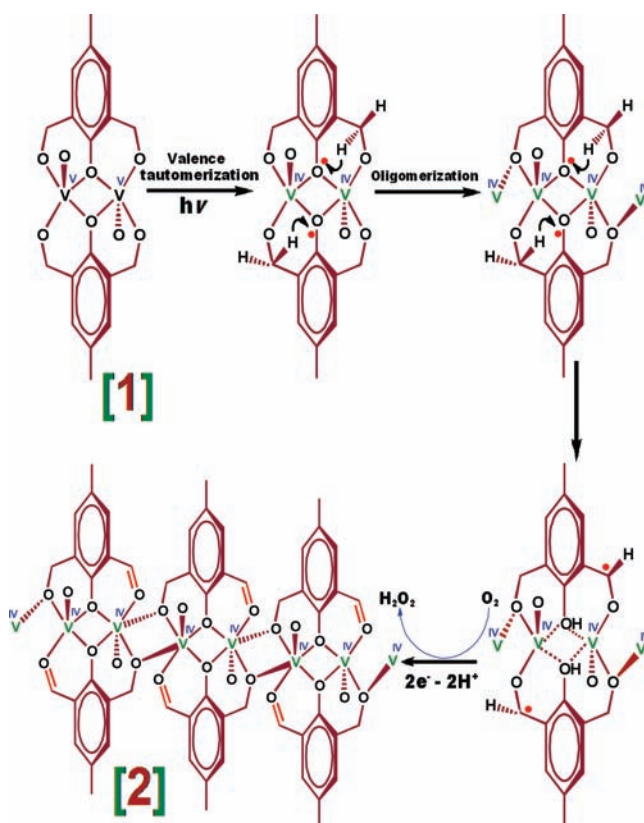
When stored in dark or kept in an inert atmosphere of argon, **1** is stable for an indefinite period of time. Control experiments have also established that simultaneous exposures to white light and aerial oxygen are mandatory to initiate the above transformation. To understand the underlying mechanism, we followed the progress of this solid-state reaction through a day-to-day analysis of the change in crystallographic data of **1** during the course of its transformation to **2**. Figure S2 (Supporting Information) displays a collection of three such molecular views

obtained when the aerial exposure time is gradually increased, while Table 1 summarizes the changes in the relevant metrical parameters. A closer look at Table 1 reveals some interesting trends especially those occur during the first 14 days of exposure. These include, a perceptible decrease in the C1−O2 (phenoxido) bond length during this period with concomitant increase in the V−O4 terminal bond length (due to the formation of vanadium(IV) from vanadium(V)).[7] This provides a hint to the generation of a phenoxyl radical,[9] probably through a light-induced valence-tautomeric equilibrium process, which we believe, is initiating this transformation (Scheme 1). The resultant increase in vanadium ionic radius in going from vanadium(V) to vanadium(IV) makes the oligomerization credible through bridging via V2−O3 bond formation (see Table 1). The concluding step is the oxidation of an alcoholate group to an aldehyde (as revealed from the more pronounced decrease in C7−O1 bond length after the initial two weeks of exposure) by molecular oxygen, which in turn is converted to H_2O_2 through a mechanism as represented by eq 1 and elaborated in Scheme 1. Due to sluggish nature of this heterogeneous reaction, the detection of H_2O_2 remained elusive despite our best efforts.

$$RCH_2OH + O_2 \rightarrow RCHO + H_2O_2 \qquad (1)$$

The progress of this reaction has been followed also by EPR spectroscopic measurements (Figure 3), which provide support to the mechanism of this light-induced process. The EPR spectrum of **1** recorded after exposure to white light for a day shows a sixteen-line axial spectrum (Figure 3a) with $g_\parallel = 1.931$; $g_\perp = 1.977$; $A_\parallel = 170 \times 10^{-4}$ cm^{-1}; and $A_\perp = 60 \times 10^{-4}$ cm^{-1}, typical of a magnetically diluted solid vanadium(4+) species doped in a diamagnetic host lattice.[10] The observed EPR spectrum supports the formation of vanadium(IV) in trace quantity through a process of valence tautomerism. As the reaction proceeds more toward the completion, incremental amounts of vanadium(IV) are generated in the solid sample to provide magnetically concentrated species,
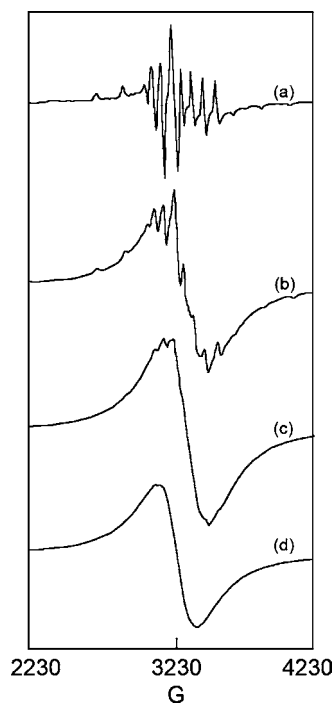
that show gradual loss of spectral resolution due to the effect of dipolar broadening (Figures 3b and 3c).[10] The final product **2** is an antiferromagnetically coupled solid with a subnormal magnetic moment of 1.81 μ_B (per binuclear unit) at room temperature, while its EPR spectrum (Figure 3d) displays a broad isotropic feature with $\langle g \rangle = 1.967$. The observed spectral changes support the formation of vanadium(IV) initially on the surface of the crystal and subsequently moves inward at a rate controlled by the diffusion of molecular oxygen in to the bulk.

In summary, we have reported here an interesting example of a single crystal-to-single crystal transformation involving a binuclear alcoholato−vanadium(V) compound (**1**) to an oligomeric aldehyde-coordinated vanadium(IV) product (**2**). This irreversible topotactic transformation is apparently triggered by photoinduced generation of phenoxyl radical that initiates an internal redox process where vanadium(V) is reduced to vanadium(IV) at the expense of a two-electron ligand-based oxidation from an alcoholate to an aldehyde. The additional equivalent of an electron being released is scavenged by molecular oxygen, yielding hydrogen peroxide. Unfortunately, we are unable to detect the liberated hydrogen peroxide in spite of our best efforts due to the sluggish nature of this heterogeneous reaction. In this transformation, a reactant in the gaseous state (molecular oxygen) reacts with a crystalline solid to generate another crystalline compound along with a product (hydrogen peroxide) that is liberated to the atmosphere. This remarkable observation reported here is probably the first of its kind.

Supporting Information Available: Synthesis, characterization details, tables of relevant crystallographic data, Figures S1 and S2, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 3. Changes in the EPR spectral pattern of **1** during its exposure to white light for (a) one day (amplitude 100), (b) 8 days (amplitude 25), (c) 14 days (amplitude 25), and (d) 35 days (amplitude 25).

References

(1) (a) Tanaka, K.; Toda, F.; Mochizuki, E.; Yasui, N.; Kai, Y.; Miyahara, I.; Hirotsu, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 3523. (b) Papaefstathiou, G. S.; Zhong, Z.; Geng, L.; Macgillivray, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 9158. (c) Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769. (d) Xiao, J.; Yang, M.; Lauher, J. W.; Fowler, F. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 2132. (e) Ouyang, X.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 12400. (f) Natarajan, A.; Tsai, C. K.; Khan, S. I.; McCarren, P.; Houk, K. N.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 9846.

(2) (a) Cheng, K.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 8102. (b) Kim, J. H.; Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 87. (c) Hu, C.; Englert, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 2281. (d) Zhang, J.-P.; Lin, Y.-Y.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 14162. (e) Cheng, X.-N.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* **2007**, *129*, 15738.

(3) (a) Han, Y.-F.; Jia, W.-G.; Lin, Y.-J.; Jin, G.-X. *Angew. Chem., Int. Ed.* **2009**, *48*, 6234. (b) Ohmari, O.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 16292. (c) Lee, E. Y.; Suh, M. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2798. (d) Armentano, D.; DeMunno, G.; Mastropietro, T. F.; Julve, M.; Lloret, F. *J. Am. Chem. Soc.* **2005**, *127*, 10778. (e) Toh, N. L.; Nagarathinam, M.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2237.

(4) (a) Rammel, A.; Brisach, F.; Henry, M. *J. Am. Chem. Soc.* **2001**, *123*, 5612. (b) Ako, A. M.; Hewitt, I. J.; Mereacre, V.; Clérac, R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4926. (c) Lampropoulos, C.; Abboud, K. A.; Stamatatos, T. C.; Christou, G. *Inorg. Chem.* **2009**, *48*, 813.

(5) (a) Chatterjee, P. B.; Bhattacharya, K.; Kundu, N.; Choi., K.-Y.; Clérac, R.; Chaudhury, M. *Inorg. Chem.* **2009**, *48*, 804. (b) Chatterjee, P. B.; Abtab, S. M. T.; Bhattacharya, K.; Endo, A.; Teat, S. J.; Chaudhury, M. *Inorg. Chem.* **2008**, *47*, 8830. (c) Chatterjee, P. B.; Bhattacharya, S.; Audhya, A.; Choi, K.-Y.; Endo, A.; Chaudhury, M. *Inorg. Chem.* **2008**, *47*, 4891, and references therein.

(6) See Supporting Information.

(7) Nanda, K. K.; Mohanta, S.; Ghosh, S.; Mukherjee, M.; Helliwell, M.; Nag, K. *Inorg. Chem.* **1995**, *34*, 2861.

(8) Keating, A. E.; Garcia-Garibay, M. A. Photochemical Solid-to-Solid Reactions. In *Organic and Inorganic Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1998, Vol. 2, pp 195−248.

(9) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **2001**, *50*, 151.

(10) Mabbs, F. E.; Collison, D. *Electron Paramagnetic Resonance of d Transition Metal Compounds*; Elsevier: Amsterdam, The Netherlands, 1992.