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A Hexanuclear Mixed-Valence Oxovanadium(IV,V) Complex as a Highly Efficient Alkane Oxidation Catalyst

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Supporting Information

ABSTRACT: The new hexanuclear mixed-valence vanadium complex $[V_3O_3(OEt)(ashz)_2(\mu\text{-}OEt)]_2$ (**1**) with an N,O-donor ligand is reported. It acts as a highly efficient catalyst toward alkane oxidations by aqueous H_2O_2. Remarkably, high turnover numbers up to 25000 with product yields of up to 27% (based on alkane) stand for one of the most active systems for such reactions.

Vanadium exhibits a wide range of oxidation states (from −3 to +5), of which +3 to +5 are biologically important,[1] whereas +4 and +5 are the most common ones and easily switch under aerobic conditions, depending, e.g., on the basicity of the ligand and pH. The study of mixed-valence vanadium complexes is receiving much attention, and dinuclear oxovanadium(IV,V) species containing the $[V_2O_3]^{3+}$ core represent the largest class in accordance with their favorable thermodynamic stability and ease of formation from the constituent $[V^{IV}O]^{2+}$ and $[V^{V}O_2]^{+}$ ions.[2] A few trinuclear and tetranuclear mixed-valence vanadium complexes have been described,[3] but, to our knowledge, there is no report on mixed-valence oxovanadium complexes with nuclearities higher than 4.

On the other hand, the ability to show different oxidation states and coordination numbers, and the high oxygen affinity, renders vanadium complexes as versatile catalysts for the oxidation of aromatic, olefinic, and even saturated hydrocarbons.[4] The oxidative functionalization of inert alkanes (relatively cheap and abundant raw materials) to more valuable organic products is of particular importance and industrial significance.[4a−e] A mixed-valence and/or a polynuclear vanadium center can help to stabilize intermediates formed during the catalytic cycle, as was recently disclosed by density functional theory (DFT) calculations.[4k] In particular, oligovanadates efficiently catalyze alkane oxidation by H_2O_2 in neutral CH_3CN, whereas the simple monovanadates and other vanadium catalysts require the presence of an acid cocatalyst.[4c,d,i−l]

For such a purpose, *N*-acetylsalicylhydrazidate (H_3ashz) was selected as the *pro*-ligand [see the Supporting Information (SI), Scheme S1a,b] because it bears two potential chelating moieties with different negative charges that can show distinct affinities for different vanadium oxidation states (IV and V): a mononegative NO coordination pocket (SI, Scheme S1c, A) and a dianionic NO_2 one (SI, Scheme S1c, B), respectively. It undergoes enolization in solution and, upon deprotonation, can act as a trinegative chelator able to simultaneously encapsulate two metal ions (SI, Scheme S1c).

When H_3ashz is treated with $VOSO_4\cdot 3H_2O$ in ethanol under reflux, the hexanuclear mixed-valence vanadium(V/IV/V/V/IV/V) complex $[V_3O_3(OEt)(ashz)_2(\mu\text{-}OEt)]_2$ (**1**) is formed (SI, Scheme S1d). The molecular structure of **1** was authenticated by single-crystal X-ray diffraction (Figure 1) and reveals two trinuclear vanadium assemblies bound by two exogenous ethoxide bridging groups, which coordinate to V2 and V2^i atoms, forming a central V_2O_2 core. The crystallographically imposed inversion center is located in the center of this core, ultimately leading to the hexanuclear arrangement. There are three different sets of VO centers in **1** with distinct donor groups around the metal cations. The terminal V1 (or V1^i) center presents a perfect square-pyramidal geometry ($\tau_5 = 0.00$; SI, Table S2) with a N_1O_3 basal plane where one of the O atoms comes from an ethoxide moiety; the arrangement around V3 (or V3^i) is also square-pyramidal, although with a slight distortion ($\tau_5 = 0.14$; SI, Table S2), but the basal plane is now of the $N_2(O_{ashz})_2$ type; finally, the V2 (or V2^i) metal atom of the central core presents a distorted octahedral geometry by means of a N_1O_3 environment in the equatorial plane and oxide and the μ-ethoxide group in the axial sites. The structure of **1** can be viewed as containing an edge-sharing $V_2O_{10}N_2$ bioctahedron, with two terminal oxide ligands placed on opposite sides (anti) of the V_2O_2 core. The distinct ashz^{3-} charge contributions to the metals (depending on pockets A or B; SI, Scheme S1c) and the ethoxide ligands suggest V1 (or V1^i), V2 (or V2^i), and V3 (or V3^i) with oxidation states 5+, 5+, and 4+, respectively. The presence of $V^{IV}O$ centers is confirmed by typical electron paramagnetic resonance data (SI, Figure S1). V═O bond lengths (SI, Table S2) fall in the normal range, and the differences are within the standard deviations.

The electrochemical study of **1**, in a 0.2 M $[^nBu_4N][BF_4]$/tetrahydrofuran solution, is consistent with the presence of a mixed-valence vanadium(V/IV/V/V/IV/V) species (SI, Figure S2).

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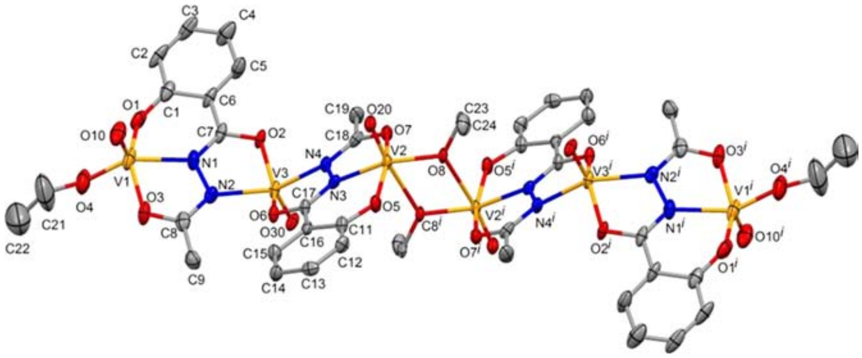

Figure 1. ORTEP diagram of **1** with an atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms were omitted for clarity. Symmetry operation to generate equivalent atoms: i, $1 - x$, $1 - y$, $-z$.

We have found that **1** in the presence of 2-pyrazinecarboxylic acid (PCA) efficiently catalyzes the oxidation of alkanes by aqueous H_2O_2 in CH_3CN at 50 °C to the corresponding alcohols and ketones, via formation of alkyl hydroperoxides as primary oxidation products (SI, Scheme S2). Remarkably, high values (up to ca. 25000) of the turnover number (TON, mol of products/mol of **1**) are achieved, and product yields can reach 27%.

The dramatic effect of PCA is shown in Figure 2, with the reaction becoming much faster and leading to much higher yields and TONs (e.g., 5% vs 27% and 460 vs 2460 after a 2 h reaction, for $[\mathbf{1}] = 5 \times 10^{-5}$ M, in the absence or presence of PCA, 5×10^{-3} M). With an increase in the concentration of **1** (to 5×10^{-4} M), the effect of PCA is not so pronounced, i.e., 16% vs 25% for the total product yield in cyclohexane oxidation in the absence or presence of PCA, respectively (SI, Figure S3). The **1**/PCA/H_2O_2 system is also efficient for the oxidation of cyclooctane (SI, Figure S4, curve *2*; 28% total yield of cyclooctanol and cyclooctanone, TON 2560).

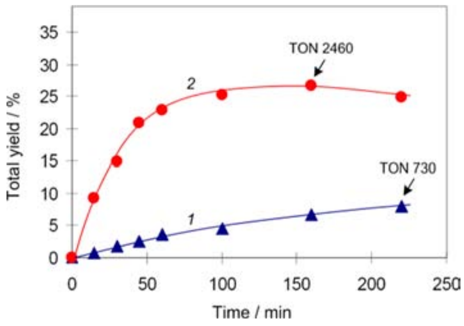

Figure 2. Effect of the acid cocatalyst and time on the total yield of cyclohexanol and cyclohexanone (%, based on alkane) in the oxidation of C_6H_{12} (0.46 M) by H_2O_2 (2.2 M) at 50 °C in CH_3CN catalyzed by **1** (5×10^{-5} M), in the absence (curve 1) or presence of PCA (0.005 M, curve 2). The experimental error is ±5%.

We have evaluated the effect of the catalyst concentration on the reaction rate of oxygenate species formation and on the corresponding total yield (Table 1 and SI, Figure S5). At a higher concentration of **1** (5×10^{-4} M), the reaction proceeds very rapidly, achieving a maximum yield of oxygenated products (25%) after 30 min. At 5×10^{-5} M concentration of **1**, there is slight deceleration of the reaction rate, although oxidation is still very efficient (27% total yield, TON 2460, after ca. 1.5 h). The decrease of the catalyst amount to 10^{-5} and 10^{-6} M results in a proportional reaction rate drop but with preservation of the catalyst efficiency, which corresponds to unprecedentedly high (for any vanadium-containing catalyst in alkane oxidation) TONs of 8370 and 24800, still with reasonable total product yields of 18.2% and 5.4%, respectively (Table 1).

Table 1. Oxidation of Cyclohexane by H_2O_2 Catalyzed by 1/PCA[a]

no.	**1** [M]	time [min]	yield [%][b] ROOH	OL	ON	total	TON[c]
1	5×10^{-4}	34	5.6	10.0	9.6	25.2	232
2	5×10^{-5}	160	0	10.3	16.4	26.7	2460
3	10^{-5}	300	0	4.9	13.3	18.2	8370
4	10^{-6}	500	0	1.9	3.5	5.4	24800

[a] Reaction conditions: C_6H_{12} (0.46 M), PCA (0.005 M), H_2O_2 (50% aqueous, 2.2 M), CH_3CN (up to 5 mL total volume), 50 °C. [b] Based on C_6H_{12}, calculated from gas chromatographic analysis after treatment of the reaction mixture with PPh_3 (the experimental error is ±5%); ROOH stands for cyclohexyl hydroperoxide, OL for cyclohexanol, and ON for cyclohexanone. [c] Total TON corresponds to moles of products per mole of catalyst.

Because the maximum reaction rate of cyclohexane oxidation (W_{max}) has a first-order dependence on [**1**] (in the 1×10^{-6}–5×10^{-5} M range; SI, Figure S6), the involvement of one vanadium-containing species in the mechanism can be proposed.

In order to elucidate the type of mechanism, we evaluated the selectivity parameters in the oxidations of different linear and branched alkanes, catalyzed by **1** both in the presence and in the absence of PCA (SI, Table S3). The regioselectivies and bond selectivities of *n*-heptane and methylcyclohexane oxidations by **1** (1:6:6:6 and 1:6:15, respectively) are close to those observed using **1**/PCA (1:7:7:6 and 1:6:13). The stereoselectivity parameters of *cis*- and *trans*-dimethylcyclohexane oxidation by **1** and **1**/PCA are also similar (in the 0.5–0.7 range), and their values (as well as those of the above selectivities) are comparable to those found for different V/H_2O_2 and other transition-metal catalytic systems that oxidize alkanes with participation of hydroxyl radicals.[4a−d,j,k] In addition, a strong inhibiting effect on the formation of oxygenate species was observed when oxidation reactions were run in the presence of either oxygen- or carbon-centered radical quenchers, Ph_2NH or $CBrCl_3$ (SI, Figure S7). In the latter case, the formation of $C_6H_{11}Br$ (ca. 39% after 2 h) was observed, while the total yield of oxygenated products dropped to 0.8% (or 5% in the presence of Ph_2NH) versus 25% under standard conditions. Thus, on the basis of the selectivity parameters and kinetic data, we can conclude that **1** and **1**/PCA operate via a common type of mechanism, with involvement of $HO^\bullet$ radicals.

The mixed-valence character of **1** can be favorable because it exhibits both 4+ and 5+ vanadium oxidation states, which are required[4a−d,j,k] for the metal-promoted generation of $HO^\bullet$ from H_2O_2. However, because **1** and **1**/PCA exhibit different efficiencies and kinetic rates under identical reaction conditions, different catalytic species can be involved. PCA can possibly displace one or more N,O-donor ligands in **1**,[4c,d,j] as suggested by electrospray ionization mass spectrometry (see the SI), thus resulting in the formation of catalytically more active species than **1** itself. Besides, PCA can play a key role as a stabilizer in hydrogen-transfer steps in the "water-assisted" mechanism of free-radical generation, as was recently disclosed, based on DFT calculations, for H_2O_2/VO_3^-/PCA-catalyzed alkane oxidation.[4j] The acidity of the reaction medium (due to the presence of PCA or any other acid) is crucial for the formation of oligovanadates, which reveal higher catalytic activity without the requirement of an additive, in contrast to a simple monovanadate.[4k] The high activity of the polynuclear complex **1** suggests that multinuclearity can be a favorable feature with a more general character, valid for vanadium centers of other types, besides vanadates.

In summary, a unique hexanuclear oxovanadium compound has been synthesized and fully characterized, revealing the first example of a high-nuclearity mixed-valence vanadium complex bearing an N,O-donor ligand. It exhibits remarkably high activity toward mild alkane oxidations by H_2O_2, in the presence of a PCA cocatalyst, leading to good yields and exceptionally high TONs (up to ca. 25×10^3 or ca. 4.2×10^3 if recalculated for the number of V atoms), with the latter being unprecedented for any vanadium-catalyzed alkane oxidations by H_2O_2, including also an efficient state-of-the-art $VO_3^-/$PCA/H_2O_2 system.[4a−d] Such a high activity of **1** deserves further exploration and elucidation. The extension of this type of study to the synthesis and catalysis of other multinuclear mixed-valence vanadium(IV/V) complexes, as well as to other alkanes, and a detailed kinetic and mechanistic investigation will be pursued.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files of **1** (CCDC 884049) in CIF format, experimental details, Figures S1−S7, Schemes S1 and S2, and Tables S1−S3. 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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