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Multielectron Redox Process of Vanadium Complexes in Oxidation of Low-Coordinate Vanadium(III) to Oxovanadium(V) with Dioxygen

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Recent interest in the chemistry of oxometal complexes (LM═O, L = ligand) has been stimulated by their significance as reactive intermediates of oxygenase and oxidase enzymes,[1] as new types of metallomesogens tuning intermolecular interactions,[2] and as one of the essential structures for protonation-triggered multielectron transfers at single electrode potentials.[3] Of greatest importance are the synthetic applications to multielectron redox catalysts. A typical example is the epoxidation of olefins catalyzed by (tetramesitylporphyrinato)ruthenium(II) in which O_2 is reduced to epoxide by the four-electron redox process of ruthenium ($O{=}Ru^{VI}{=}O \rightleftharpoons Ru^{II} + O_2$).[4] As a new type of multielectron mediated system, we have been studying the oxovanadium-catalyzed O_2-oxidative polymerization of diphenyl disulfide in strongly acidic conditions which provides a convenient synthesis of poly(*p*-phenylene sulfide), an important engineering plastic.[5] We previously reported that a model complex of the catalyst, $V^{IV}O$(salen), (H_2salen = *N,N′*-ethylenebis(salicylideneamine)) forms a *μ*-oxo dinuclear vanadium complex $[(salen)V^{IV}OV^{IV}(salen)]^{2+}$ (VOV^{2+}) in strongly acidic non-aqueous media.[6] Here we describe the multielectron transfer process from the reduced vanadium(III) complex (VOV^{+}) to O_2, which not only reveals the O_2-oxidation mechanism but also provides an additional insight into the unique chemistry of vanadium with possible relevance to metal monooxygenases. The product was a dimeric $[V^{IV}OV^{V}O]^{+}$ cation whose redox state was confirmed by the crystal structure analysis.

Our studies on the vanadium-catalyzed O_2-oxidative polymerization of organosulfur compounds led us to examine the vanadium-mediated electrochemical reduction of O_2. The redox potential of the VOV^{2+} complex is located at 0.44 V vs Ag/AgCl in CH_2Cl_2,[7] and controlled-potential reduction at 0.3 V under N_2 consumed one electron per mole of complex as expected for quantitative reduction to VOV^{+} (eq 1).[6] The

$$[(salen)V^{IV}{-}O{-}V^{IV}(salen)]^{2+} + e^{-} \rightarrow [(salen)V^{IV}{-}O{-}V^{III}(salen)]^{+} \quad (1)$$

stoichiometric formation of the low-coordinate vanadium(III)[8] prompted us to examine the reaction with O_2. Thus, 100 *μ*M VOV^{2+} in 25 mL of CH_2Cl_2 containing 0.1 M tetrabutylammonium tetrafluoroborate was subjected to controlled potential reduction at 0.4 V under N_2 to prepare the solution of VOV^{+}, and the resulting solution was exposed to O_2 gas. The oxygenated product was crystallized after anion-exchange by the addition of an excess amount of tetrabutylammonium triiodide and allowing the solution to stand for several days.[9] X-ray diffraction studies of the crystallized product revealed that it is composed of $[(salen)VOVO(salen)]^{+}$ cations and I_3^{-} anions (Figure 1).[10] The structure consists of two crystallographically independent molecules per asymmetric unit named A and B in Figure 1. Although the arrangements near vanadium in the two molecules were similar, the salen ligand aligned differently. Molecule A bears an unusual salen coordinating mode with the bridging ethylenediimine groups being aligned at the same side. The V(2) atom in molecule A, surrounded by the four coordinating atoms of a salen ligand (N_2O_2), extends 0.270 Å above the best N_2O_2 least-squares plane. The arrangement around V(2) is fairly distorted octahedral (O(3)−V(2)−O(6): 174.0(4)°). In contrast, the V(1) atom lying as much as 0.550 Å above the N_2O_2 plane and O(3) being 1.622(7) Å beyond the V(1) atom represent a typical square-pyramidal coordination structure. It is known that the oxidation state of the vanadium atom is hardly reflected in the V═O bond length.[11] Nevertheless we can notice that the 1.573(8) Å V(2)−O(6) distance of the $VOVO^{+}$ complex is closer to the V═O bond length of oxovanadium(V) complexes such as those of VO(salen)ClO_4

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(7) The formal potential of the ferrocene/ferrocenium couple was 0.34 V vs this reference electrode.

(8) The product of the electrochemical reduction of the $[V^{IV}OV^{IV}]^{2+}$ dimer showed a weak and broad intervalence transition band at $\lambda_{max} = 7.2 \times 10^3$ cm^{-1} with half-band width of 3.0×10^3 cm^{-1} due to the mixed-valent state ($[V^{IV}OV^{III}]^{+}$). IR (cm^{-1}, in CH_2Cl_2): 978. UV (λ_{max}, nm, in CH_2Cl_2): 365, 280, 240. FABMS (*m/z*): 650.

(9) Anal. Calcd for $C_{32}H_{28}N_4O_6V_2I_3$ ($M = 1047.19$): C, 36.70; H, 2.70; N, 5.35%. Found: C, 36.59; H, 2.67; N, 5.14%. IR (KBr): 1620, 1547, 1470, 1445, 1391, 1335, 1152, 1128, 982, 936, 910, 856, 818, 804, 754, 660, 631 cm^{-1}. FABMS (*m/z*): 1047, 667. UV (λ_{max}, nm, in CH_2Cl_2): 240, 282, 365. ESR (eight-line signal, in CH_2Cl_2): $g_0 = 1.98$, $A_0 = 99.1$ G. Both near-infrared spectrum (with no intervalence transition band) and ESR spectrum confirmed the localized mixed-valent state of the $[V^{IV}OV^{V}O]^{+}$ cation. It is likely that the structure of the dimer persists in CH_2Cl_2 solution, since ESR and UV data for the dimer are different from those obtained for an equimolar mixture of $V^{IV}O$(salen) and $V^{V}O(salen)^{+}$ in CH_2Cl_2. (ESR: $g_0 = 1.98$, $A_0 = 98.1$ G. UV (λ_{max}, nm): 250.) Moreover, in the mass spectrum of the CH_2Cl_2 solution of the dimer was detected the parent ion for the dimer (*m/z* = 667), which also supported the persistence of the structure. Further structural analysis in solution is the subject of our continuing research.

(10) Crystal data for $C_{32}H_{28}N_4O_6V_2I_3$: black, triclinic, $P\bar{1}$ (No. 2), $a = 14.973(2)$ Å, $b = 19.481(2)$ Å, $c = 14.168(2)$ Å, $\alpha = 107.00\ (1)°$, $\beta = 115.56(1)°$, $\gamma = 80.35(1)°$, $V = 3561.3(9)$ Å^3, $Z = 4$, $D_{calc} = 1.953$ g/cm^3, μ(Mo Kα) = 31.74 cm^{-1}; Rigaku AFC5S diffractometer, structure solution by direct methods, structure refinement by full-matrix least-squares techniques; final $R = 0.057$, $R_w = 0.065$. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985 & 1992).

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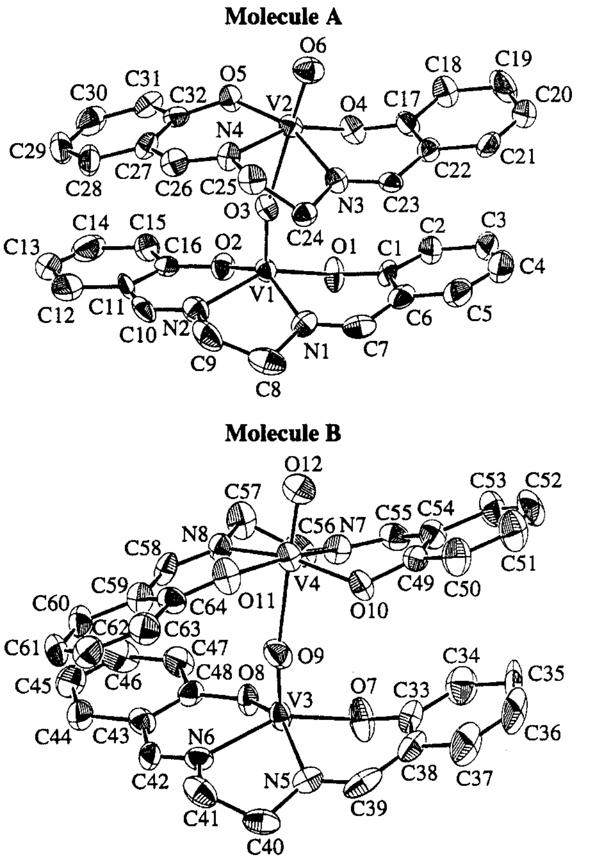

Figure 1. ORTEP view (50% probability ellipsoids) of the cations in [VOVO(salen)$_2$][I$_3$]. Selected bond length (Å) and angles (deg) for molecule B: V(3)−O(9), 1.612(8); V(3)−O(7), 1.928(8); V(3)−O(8), 1.903(7); V(4)−O(10), 1.845(8); V(4)−O(11), 1.822(8); V(4)−O(9), 2.246(8); V(4)−O(12), 1.578(8); O(9)−V(4)−O(12), 175.8(4). Deviation of vanadium atoms from the mean N$_2$O$_2$ plane (Å): V(3), 0.536; V(4), 0.262. Data for molecule A, see text.

(1.576(3) Å) and VO(salen)BF$_4$ (1.577(1) Å) than that of V^{IV}O(salen) (1.583(5) Å).[12] The vanadium−phenolate oxygen bond length is more indicative of the oxidation state since the V−O(phenolate) bond is known to shrink upon one-electron oxidation of vanadium(IV). Indeed, the alternating short V(2)−O(phenolate) bond length (V(2)−O(4), 1.831(8) Å; V(2)−O(5), 1.811(7) Å) and long V(1)−O(phenolate) length (V(1)−O(1), 1.898(7) Å; V(1)−O(2), 1.894(7) Å) support the mixed valent [V^{IV}−O−V^{V}=O]$^+$ formulation (eq 2).

$$2[(\text{salen})\text{V}^{\text{IV}}\text{—O—V}^{\text{III}}(\text{salen})]^+ + \text{O}_2 \rightarrow 2[(\text{salen})\text{V}^{\text{IV}}\text{—O—V}^{\text{V}}(\text{salen})\text{=O}]^+ \quad (2)$$

The weak axial interaction with O(3), as judged by the long V(2)−O(3) bond length (2.214(7) Å) and the V(2) atom substantially protruded from the N$_2$O$_2$ plane, is due to the low residual basicity of O(3) which is bound with a multiple bond to V(1). It is the preference of the vanadium(V) to be six-coordinate rather than five that drives the formation of the dimer.[13] The bond lengths in molecule B support the same redox state. The units of the two molecules are separated by the almost linear I$_3^-$ anion which is arranged between the unit.

The present structure of the cation is similar to that described in the pioneering work by Leigh et al.,[14] in which I$_5^-$ is involved as the counterion. The longer I$_5^-$ ion surrounded the VOVO axis and the cations were arranged in a chainlike crystal packing structure (V−O−V−O···V−O−V−O···). They concluded that, from the long V···O distance between the two VOVO cations (2.41(4) Å), that the complex is comprised of a bimetallic units. In contrast, our complex [VOVO][I$_3$] may be the first example, to our knowledge, of an oxo-bridged vanadium complex with an obvious dinuclear structure. A comparison of the two structures suggests that I$_3^-$ with shorter length and higher charge density is arranged in the proximity of the low-coordinate V(1) and V(3) atoms.

The stoichiometry of reaction 2 is reminiscent of the electroreduction of O$_2$ to H$_2$O. Oxygen incorporation from molecular O$_2$ to produce oxide is an important process in the action of metal monooxygenases, and is represented by, *e.g.*, a model containing dinuclear copper complex.[15] It is of interest that oxygenation of vanadium(III) gives oxovanadium(V) whereas multiple one-electron redox centers have been considered to be essential for the incorporation of O$_2$. This is due to the reactivity of the low-coordinate vanadium(III) and the stability of the oxovanadium(V) species. The system has significant potential in leading to the selective four-electron reduction of O$_2$ to H$_2$O in acidic medium, since VO(salen) has been confirmed to undergo deoxygenation to give V(salen)$^{2+}$ and H$_2$O in strongly acidic conditions.[6]

A further important issue is the implication of vanadium(III)/oxovanadium(V) interconversion. O$_2$ oxidation of metal complexes to oxometal complexes (LM^x + $^1/_2$O$_2$ → LM^{x+2}=O) produces a fully reduced oxo ligand, and the resulting high-valent complexes often act as multielectron redox catalysts. For example, the VO-catalyzed O$_2$-oxidative polymerization of disulfide is mediated by a vanadium(III/V) redox couple. In addition, a two-electron transfer process involved in the protonation-assisted interconversion between vanadium(III) and oxovanadium(V) might play a role in the operation of prosthetic groups mediating biological redox reactions such as those of the vanadium haloperoxidases[16] and in the unknown function of accumulated vanadium(III) in sea squirts.[17] The aprotic nonaqueous oxygenation of vanadium(III) to oxovanadium(V) species achieved in the present system may offer a possible alternative halide oxidation mechanism.

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Supporting Information Available: Tables giving atomic coordinates, equivalent isotropic thermal parameters, bond lengths and angles, nonbonded contacts out to 3.60 Å, and anisotropic displacement parameters (25 pages). Ordering information is given on any current masthead page.

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