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The first evidence for activation of exogenous O_2 on a vanadium(IV) center: synthesis and characterization of a peroxo vanadium(V) complex with hydrotris(3,5-diisopropylpyrazol-1-yl)-borate

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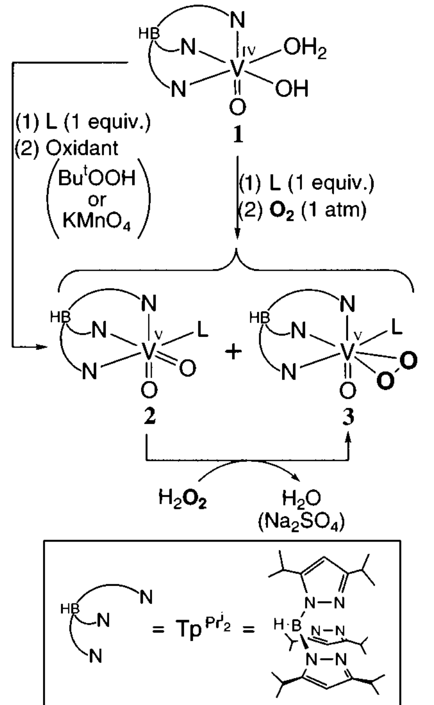
Reaction of a vanadium(IV) hydroxo complex bearing hydrotris(3,5-diisopropylpyrazol-1-yl)borate ($\mathrm{Tp^{Pr^i_2}}$) with O_2 results in reductive O_2 activation to give $\mathrm{Tp^{Pr^i_2}V^V(O)(\eta^2\text{-}O_2)(L)}$; the first example of the formation of a peroxo vanadium complex from molecular oxygen.

Reductive O_2 activation ($O_2 \longrightarrow O_2^- \longrightarrow O_2^{2-} \longrightarrow 2 \times O^{2-}$) *via* oxidative addition of molecular oxygen to a transition metal center is a fundamental process in various synthetic O_2 oxidation reactions and physiological O_2 metabolism. Therefore, research into the reactivity of transition metal complexes toward O_2 activation and the characterization of the resulting peroxo complexes is essential to the understanding of the synthetic and metabolic O_2 activation mechanisms.[1] It is known that vanadium–peroxo species take part in various catalytic oxidations ranging from industrial processes to enzymatic reactions.[2] However, the oxidant used in most of these processes (including halide oxidation by haloperoxidases) is not O_2 but ROOH (R = H, alkyl); only a limited number of aerobic oxidation reactions by vanadium catalysts have been reported. Moreover, the role of the vanadium center in aerobic oxidation processes is proposed to assist the autoxidation reaction (*i.e.* degradation of the alkylhydroperoxides to induce radical chain reaction).[3] In addition, previously reported vanadium(V)–peroxo complexes were prepared by the reaction of appropriate V(V)–oxo or –hydroxo precursors with ROOH,[2] and no examples of the formation of a peroxo complex *via* incorporation of an external O_2 molecule was known to date.[4] In this communication, we report the first evidence for the activation of exogenous O_2 on V(IV) centers resulting in formation of V(V)–peroxo species.†

We have been investigating the peroxo and related complexes of various first- and second-row, late transition metals (Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd) with the hindered hydrotris(pyrazolyl)borate ligands ($\mathrm{Tp^R}$) in order to obtain comprehensive insights into the role of metal ions in various oxidation processes.[5] Recently, our research target has been extended to the early transition metals, and a V(IV)–hydroxo complex with hydrotris(3,5-diisopropylpyrazol-1-yl)borate ($\mathrm{Tp^{Pr^i_2}}$), $\mathrm{Tp^{Pr^i_2}V^{IV}(O)(OH)(OH_2)}$ **1**, has been synthesized and characterized successfully.[6] When a toluene solution of **1** was exposed to O_2 (1 atm) in the presence of 1 equiv. of 3,5-diisopropylpyrazole ($\mathrm{Pz^{Pr^i_2}H}$) ‡ at room temperature, the purple solution changed to a dark red one within 2 h. NMR (^{51}V, ^{13}C and ^{1}H) and IR spectra of the resulting products clearly indicated the existence of two sets of $\mathrm{Tp^{Pr^i_2}V^V(Pz^{Pr^i_2}H)}$ moieties in a 1 : 1 : molar ratio and, in addition, two sets of *ν*(V=O) and *ν*(O–O) vibration bands appeared in the 960–890 cm^{-1} region (in the IR region). Finally, these two products were identified as mononuclear V(V)-*cis*-dioxo and –oxo–peroxo complexes, $\mathrm{Tp^{Pr^i_2}V^V(O)_2(Pz^{Pr^i_2}H)}$ **2** and $\mathrm{Tp^{Pr^i_2}V^V(O)(\eta^2\text{-}O_2)(Pz^{Pr^i_2}H)}$ **3**, respectively, by comparison of the spectral data with those of the independently prepared authentic samples whose molecular structures were successfully determined by X-ray crystallography (see below).§

An authentic sample of **2** was synthesized by chemical oxidation of **1** with Bu^{t}OOH or $KMnO_4$ in the presence of 1 equiv. of the pyrazole ligand ($\mathrm{Pz^{Pr^i_2}H}$), and subsequent dehydrative condensation of the isolated **2** with H_2O_2 (in the presence of Na_2SO_4 as dehydrating reagent) yielded the corresponding V(V)–oxo–peroxo complex **3** (Scheme 1).¶ The pale yellow dioxo complex **2** involves a slightly distorted octahedral vanadium center coordinated by two terminal oxo ligands in *cis* configuration [Fig. 1(a)]. The structural and spectral features of **2** [(*i*) somewhat long V=O lengths: V–O(1) 1.621(3), V–O(2) 1.636(3) Å, (*ii*) elongation of two of the three V–$\mathrm{N_{Tp}}$ bond lengths *trans* to the oxo ligands are due to the strong *trans* effect from the terminal oxo ligands, and (*iii*) relatively low *ν*(V=O) vibration frequencies (921 and 893 cm^{-1})] are similar to those found for the previously reported V(V)–*cis*-dioxo complexes.[7]



Scheme 1

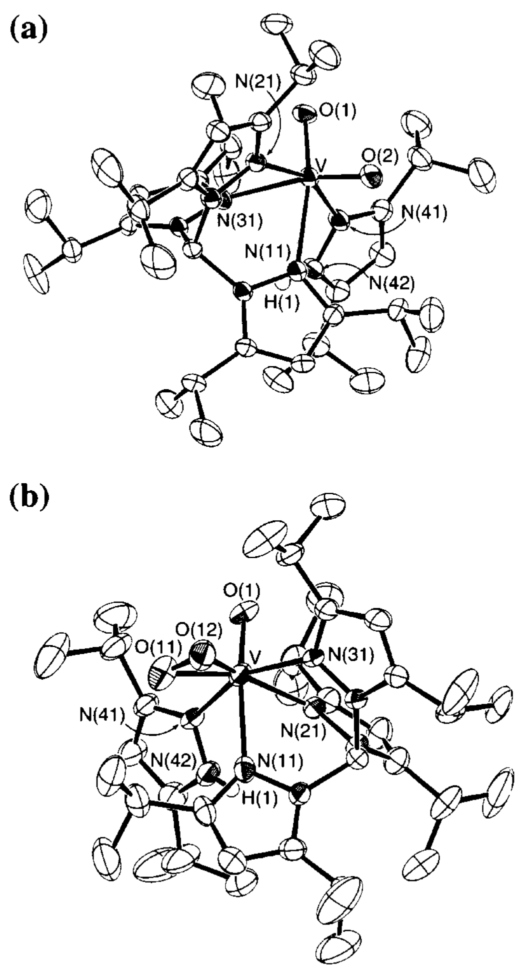


Fig. 1 Molecular structures of $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}\mathrm{V(O)_2(Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H)}$ **2** (a) and $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}\mathrm{V(O)(\eta^2{-}O_2)(Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H)\cdot THF}$ **3**·THF (b) drawn at the 50% probability level. All hydrogen atoms except those attached to the nitrogen atoms [N(42)] of the coordinating pyrazole ligands (**2** and **3**), the disordered carbon atoms of one of the three 5-Pr^{i} groups in the $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}$ ligand and the THF solvate (**3**) are omitted for clarity. Selected bond lengths (Å) and angles (°): (a) *cis*-dioxo complex **2** V–O(1) 1.621(3), V–O(2) 1.636(3), V–N(11) 2.324(5), V–N(21) 2.203(5), V–N(31) 2.122(5), V–N(41) 2.161(5), O(1)–V–O(2), 103.8(1); (b) oxo–η^2–peroxo complex **3** O(11)–O(12) 1.379(6), V–O(1), 1.603(4), V–O(11), 1.862(5), V–O(12), 1.887(5), V–N(11) 2.324(5), V–N(21) 2.203(5), V–N(31) 2.122(5), V–N(41) 2.161(5); O(11)–V–O(12), 43.2(2).

The red peroxo complex **3** has a seven-coordinated pentagonal-bipyramidal metal center containing an η^2-peroxo ligand [V–O(11) 1.862(5), V–O(12) 1.887(5) Å; O(11)–V–O(12) 43.2(2)°], and the overall structures of **2** and **3** are very similar when it is assumed that the peroxo ligand occupies a single coordination site [Fig. 1(b)]. The distance from the vanadium center to the terminal oxo ligand [V–O(1) 1.603(4) Å, *ν*(V=O) 947 cm^{-1}] is shorter than those found for the dioxo complex **2**. The relatively short O–O length [O(11)–O(12) 1.379(6) Å] is almost at the shortest end of the typical range for the O–O distances of peroxide ligands,[8] and is indicated by the relatively high *ν*(O–O) value of 960 cm^{-1}. Retention of the side-on bound peroxo ligand in solution is supported by a UV-vis spectrum of a toluene solution involving the peroxo-to-vanadium charge-transfer band around 495 nm (ε = 280 M^{-1} cm^{-1}).[2]

The O_2 activation on the V(IV) center of the hydroxo complex **1** was evidenced by a labeling experiment with $^{18}O_2$ and an external substrate oxidation ability. Of the four characteristic vibrations [*ν*(O–O) and *ν*(V=O), see above] of a reaction mixture of **1** and O_2, only the *ν*(O–O) band at 960 cm^{-1} disappeared upon treatment with $^{18}O_2$ [overlapped with the tail of the *ν*(V=O) peak at 893 cm^{-1} (**2**); observed *ν*(^{18}O–^{18}O) value = 900 cm^{-1} in the sample prepared by the reaction of **2** with $H_2{}^{18}O_2$], and the remaining three *ν*(V=O) bands were not shifted. We thus conclude that the peroxo ligand in **3** arises from the external dioxygen molecule and the origin of the terminal oxo ligands in both **2** and **3** is the oxygen atoms of the oxo and the hydroxo ligands in **1** (not O_2). Trapping of the external O_2 molecule as the peroxide (=$O_2{}^{2-}$) ligand on the vanadium center (*i.e.* formation of **3**) indicates that the present aerobic oxidation of **1** is clearly different from the usual 4e$^-$ oxidation process of $[\mathrm{V^{IV}({=}O)}]^{2+}$ compounds yielding the vanadium(V)–dioxo compounds [eqn. (1)].[2]

$$4[\mathrm{V^{IV}({=}O)}]^{2+} + 2\mathrm{H_2O} + \mathrm{O_2} \longrightarrow 4[\mathrm{V^{V}({=}O)_2}]^{+} + 4\mathrm{H}^{+} \quad (1)$$

Remarkably, the V(IV)–hydroxo complex **1** showed aerobic PPh_3 oxygenation activity [under 1 atm O_2, r.t., reaction time: 30 min, yield of O=PPh_3: 150% (based on **1** in the presence of 30 equiv. of PPh_3)], whereas the isolated mononuclear V(V)–η^2-peroxo complex **3** exhibited relatively low oxo-transfer activity under the same condition (yield 31% based on **3**) and the V(V)–dioxo complex **2** could not oxidize PPh_3 under any conditions. These observations supported the fact that the reductive O_2 activation was mediated by another vanadium–O_2 species formed at an initial stage of the oxygenation of **1**. In the present vanadium system, the electron donating ability of $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}$ might make the reductive O_2 activation on the vanadium(IV) center possible.[9]

In conclusion, the reductive O_2 activation took place on the V(IV) center of the hydroxo complex containing $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}$. The resulting monomeric V(V)–η^2-peroxo complex is the first example of the V(V)–peroxo complex derived from the direct oxygenation of the V(IV) precursor. Detailed investigation of the reactivities of the vanadium–peroxo species is now underway.

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Notes and references

† Abbreviations used in this paper: Tp^{R}, hydrotris(3,5-substituted-pyrazol-1-yl)borate; $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}$, hydrotris(3,5-diisopropylpyrazol-1-yl)-borate; $\mathrm{Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H}$, 3,5-diisopropylpyrazole.

‡ Reaction of **1** with O_2 in the absence of the additional $\mathrm{Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H}$ also resulted in the formation of the $\mathrm{Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H}$ containing complexes **2** and **3**, although the yields of them were quite low (>30% based on **1**) due to partial decomposition of the $\mathrm{Tp}^{\mathrm{Pr}^{i}_{2}}$ ligand providing the $\mathrm{Pz}^{\mathrm{Pr}^{i}_{2}}\mathrm{H}$ ligands.

§ Crystal data. For **2**: $C_{36}H_{62}N_8O_2BV$, $M = 700.69$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.698(10)$, $b = 20.54(2)$, $c = 22.84(1)$ Å, $\beta = 92.51(4)°$, $V = 4018(2)$ Å^3, $Z = 4$, $D_c = 1.16$ g cm^{-1}, μ(Mo-Kα) = 2.87 cm^{-1}, $T = -60$ °C, $R(Rw) = 0.043$ (0.046) (based on F) for 3613 $[I > 3\sigma(I)]$ reflections with 442 parameters. For **3**·THF: $C_{40}H_{70}N_8O_4BV$, $M = 788.80$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.171(2)$, $b = 17.458(4)$, $c = 25.12(1)$ Å, $\beta = 98.97(8)°$ $V = 4493(6)$ Å^3, $Z = 4$, $D_c = 1.17$ g cm^{-3}, μ(Mo-Kα) = 2.67 cm^{-1}, $T = -60$ °C, $R(Rw) = 0.077$, (0.068) (based on F) for 4472 $[I > 3\sigma(I)]$ reflections with 509 parameters. CCDC reference number 186/1394.

¶ Selected spectroscopic data. For **2**: IR (KBr pellet, *ν*/cm^{-1}): 3433(N–H), 2541 (B–H), 921, 893 (V=O). FD-MS: *m*/*z* 702 (M + H$^+$). UV-vis (toluene, λ/nm, ε/M^{-1} cm^{-1}): 749 (7.3). ^{51}V NMR (C_6D_6, reference; $VOCl_3$): δ 541. ^{1}H NMR (C_6D_6): δ 9.03 (1H, pyrazole N-*H*). For **3**: IR (KBr pellet, *ν*/cm^{-1}): 3436 (N–H), 2543 (B–H), 960 (^{16}O–^{16}O), 900 (^{18}O–^{18}O; prepared by rection of **2** with $H_2{}^{18}O_2$), 947 (V=O). FD-MS: *m*/*z* 718 (M + H$^+$). UV-vis (toluene, λ/nm, ε/M^{-1} cm^{-1}): 495 (280). ^{51}V NMR (C_6D_6, reference; $VOCl_3$): δ 552. ^{1}H NMR (C_6D_6): δ 8.43 (1H, pyrazole N–*H*).

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