Synthesis, Structure, and Catecholase Reaction of a Vanadate Ester System Incorporating Monoionized Catechol Chelation

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The oxidation of catechols to quinones by O_2—the catecholase reaction—is an important biochemical transformation usually catalyzed by binuclear copper.[1−3] Herein we describe an instance of the reaction mediated cleanly and quantitatively by the blue vanadate ester system **1**. All relevant species and their abbreviations are listed in Chart 1.

In the systhesis[4] of **1** from $VO(acac)_2$, H_2A, and excess catechol, the strategy[5,6] of blocking three coordination positions by a tridentate diionized ONO ligand leaving two positions for monoionized diol chelation affording an electroneutral VO^{3+} ester has been employed.

In the structure[7] of **1a** (Figure 1) we have the first authentic instance of monoionized catechol chelation to vanadium. The metal atom is displaced by 0.32 and 0.36 Å, respectively, from the excellent catecholate and O2N1O3O5 planes. The phenolic hydrogen is observed in difference Fourier maps and in IR and ^{1}H NMR.[4] The Hdbcat$^-$ C−O lengths (∼1.36 Å) are normal for the catecholate mode of binding.[8,9]

1 is indefinitely stable in the solid state. Its blue solutions (CH_2Cl_2, MeCN, and Me_2CO are convenient solvents) are also perfectly stable both in terms of redox and dissociation but only under N_2/Ar. In the presence of O_2, the solution color progressively changes finally becoming yellowish red. The original color is fully restored upon adding the relevant catechol externally. This forms the basis of the catalytic cycle drawn for the specific case of **1a** in Scheme 1 (**1b** and **1c** behave similarly). At the end of a cycle dbq and the oxo-bridged dimer **3a** can be isolated virtually quantitatively[10,11] and the lack of formation of any catechol-related product other than[12−14] dbq is also revealed in ^{1}H NMR spectra of reacting solutions. The *t*-Bu region is highlighted in Figure 2.

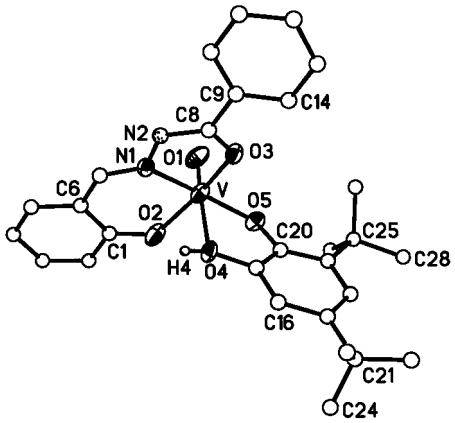

Figure 1. Perspective view of **1a** excluding hydrogen atoms except the phenolic hydrogen. Selected bond distances (Å): V−O1, 1.582(4); V−O2, 1.857(4); V−O3, 1.945(4); V−O4, 2.344(4); V−O5, 1.811(4); V−N1, 2.091(5); O4−C15, 1.361(5); O5−C20, 1.356(6). The lattice consists of dimers formed via intermolecular N2···O4, hydrogen bonds of length 2.669(8) Å.

Chart 1

Catechols, Quinones and Coligands

$C_6H_4(OH)_2$ (H_2cat); $C_6H_4O_2$ (q)
3,5-(*t*-Bu)$_2C_6H_2(OH)_2$ (H_2dbcat)
3,5-(*t*-Bu)$_2C_6H_2O_2$ (dbq)
C_6H_4(OH)CH=N-N=C(OH)Ph (H_2A^1)
p-ClC_6H_3(OH)CH=N-N=C(OH)Ph (H_2A^2)
C_6H_4(OH)CH=N-$CH_2C_5H_4N$ (HB)

Complexes

1a. VO(Hdbcat)(A^1); **1b.** VO(Hdbcat)(A^2)
1c. VO(Hcat)(A^1); **2.** VO(dbcat)(B)
3a. $V_2O_3(A^1)_2$; **3b.** $V_2O_3(A^2)_2$

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(3) Kitajima, N.; More-Oka, Y. *Chem. Rev.* **1994**, *94*, 737.
(4) Data for **1a**: a solution of $VO(acac)_2$ (0.10 g, 0.38 mmol), H_2L^1 (0.09 g, 0.38 mmol), and H_2dbcat (0.09 g, 40 mmol) in methanol (12 mL) was stirred in air for 10 min and then concentrated to 6 mL and cooled. The blue solid was filtered off and dried over P_4O_{10} in vacuo (yield, 81%). Anal. Calcd (found): C, 63.88 (63.84); H, 5.89 (5.92); N, 5.32 (5.38). UV−vis (acetone) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 600 (7410), 400 (8230). IR (KBr disk/halocarbon mull, cm^{-1}): 990 ($\nu_{V=O}$), 3450 (br, ν_{OH}). ^{1}H NMR (300 MHz $(CD_3)_2CO$, δ): 9.03 (s, C*H*═N); 6.80−7.76 (arom., 11H); 1.24, 1.59 (s, C*Me*$_3$); 11.40 (br, O*H*). ^{51}V NMR (78.8 MHz, external reference $VOCl_3$): −371 ppm. The other complexes were made similarly. Data for **1b**: anal. calcd (found): C, 59.95 (60.01); H, 5.35 (5.42); N, 4.99 (4.91). UV−vis: 610 (7640), 415 (5980). IR: 985 ($\nu_{V=O}$), 3425 (br, ν_{OH}). ^{1}H NMR: 9.00 (s, C*H*═N); 6.81−7.96 (arom., 10H); 11.49 (br, O*H*); 1.24, 1.58 (s, C*Me*$_3$); ^{51}V NMR: −350 ppm. Data for **1c**: anal. calcd (found): C, 57.97 (57.91); H, 3.62 (3.71); N, 6.76 (6.70). UV−vis: 550 (4730), 410 (5540). IR: 995 ($\nu_{V=O}$), 3410 (br, ν_{OH}). ^{1}H NMR: 9.07 (s, C*H*═N); 6.85−7.95 (arom., 13H); ^{51}V NMR: −430 ppm.
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(7) Data were collected on a Siemens R3m/V four-circle diffractometer equipped with a graphite crystal monochromator using Mo Kα (λ = 0.710 73 Å) radiation. The structure was solved by direct method (SHELXTL, Version 5.03) and refined on F^2 by full-matrix least-squares using $I > 2\sigma(I)$ data. Crystal data: monoclinic, $P2_1/n$; a = 14.336(7) Å, b = 9.713(4) Å, c = 19.524(8) Å, β = 92.71(4)°; V = 2716(2) Å^3; Z = 4; R1 = 0.0636, wR2 = 0.1350.
(8) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.
(9) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.
(10) A solution of **1a** (0.053 g, 0.10 mmol) in 25 mL of O_2-saturated 1:1 MeCN−CH_2Cl_2 was stirred in a two-necked flask fitted with a balloon filled with O_2. After **1a** had completely reacted (∼6 h), H_2dbcat (0.022 g, 0.10 mmol) was added. Two more 0.022 g increments of H_2dbcat were similarly added later (if desired many more such cycles could have been completed). Solvent was removed from the reaction mass, and the solid was dried in a vacuum and extracted with 25 mL petroleum ether (60−80 °C). The residue, **3a**, was filtered off and dried and the filtrate afforded dbq upon evaporation. The maximum possible yields of dbq and **3a** are 0.088 and 0.031 g, respectively, and we were able to achieve virtually quantitative recoveries. The complex **3a** has been fully characterized including structure determination.
(11) The reaction between **3a** and H_2dbcat can be used as a synthetic route to **1a**. An acetone solution (25 mL) of **3a** (0.10 g, 0.16 mmol) and H_2dbcat (0.075 g, 0.34 mmol) was stirred for 25 min in N_2 atmosphere and then concentrated to 10 mL and cooled. **1a** was precipitated in 82% yield.

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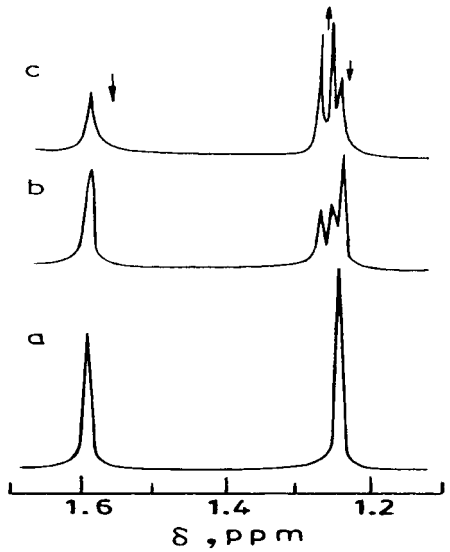
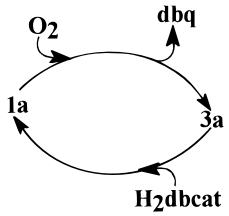
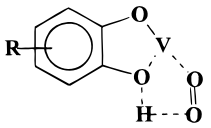


Figure 2. Time evolution ^{1}H NMR spectra (at 295K) of the two *tert*-butyl protons of **1a** in O_2-saturated acetone-d_6. In (a) dbq is absent and as the reaction progresses (b, c) its signals (δ 1.25 and 1.27) grow in intensity at the expense of bound Hdbcat$^-$ signals (δ 1.24 and 1.59).

Scheme 1



Rate studies[15] in O_2-saturated Me_2CO (295 K) have afforded the pseudo-first-order k_{obs} (s^{-1}) values: **1a**, 4.50×10^{-4}; **1b**, 2.80×10^{-4} ; **1c**, 1.10×10^{-4}. Thus electron withdrawal from either the catecholate ligand (compare **1a** and **1c**) or the A^{2-} coligand (compare **1a** and **1b**) diminishes k_{obs} clearly implying that election transfer to O_2 occurs from the intact complex and not from any dissociated catechol. The intimate mechanism of O_2 association is however unclear at present but certain observations are in order. Complex **2**[16] incorporates tridentate ONN binding by B$^-$ and diionized catecholate chelation as in related species.[17] Cyclic voltammetry in CH_2Cl_2−MeCN reveals that both **1a** and **2** display irreversible catechol oxidation with anodic peak potentials of 0.68 and 0.58 V vs SCE, respectively. Thus **2** is somewhat more easily oxidizable than **1a**, yet the former is entirely unreactive toward O_2 in solution. The phenolic hydrogen of **1** appears to have a crucial role in making **1** reactive. A plausible mode of O_2 attachment is stylized in **4**. Attachment of O_2 via hydrogen bridging has been implicated in e.g., hemoglobin[18,19] and hemerythrin[20] chemistry.



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Electron transfer from the catechol in **4** to O_2 may occur via the hydrogen bond, the metal or both. At present we do not have any direct evidence that the metal site is involved. The reaction solutions do not display any EPR signals either in fluid or in frozen conditions due to $V^{IV}O$ intermediates. Periodic examination of aqueous extracts of reacting solutions with O_2-sensitive electrodes for liberation of O_2 upon addition of peroxidase enzyme gave negative results. Thus O_2 appears to be reduced to H_2O without the intermediacy of H_2O_2 and the net result of cycle in Scheme 1 is the catecholase reaction H_2dbcat + 1/2 O_2 → dbq + H_2O. The reaction intermediate and catalyst are respectively **1a** and **3a**.

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Supporting Information Available: Tables of crystal data, complete atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameter and hydrogen atom positional and thermal parameters for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Reported oxidations of catechols by oxygen in the presence of vanadium complexes generally lead to muconic acid anhydride as the major product, quinone along with 2-pyrone being minor constituents.[8,13,14]

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(15) For **1a** the intensity of the band at 600 nm decreases with time while that of band near 400 nm due to dbq gains in intensity; isosbestic point, 415 nm. The initial O_2 concentration in the solvent determined by using an oxygen sensitive electrode is 0.90×10^{-3} M. The concentration of the complex **1** was kept $\leq 10^{-4}$ M. Pseudo-first-order condition thus apply. The plot of $\ln(A_t - A_\alpha)$ vs time (t) is excellently linear (A_t and A_α are the optical density near 600 nm at time t and after the completion of the reaction, respectively). Each complex was studied at four different concentrations.

(16) The complex was synthesized by reacting $VO(acac)_2$ with HB (Schiff base of salicylaldehyde and 2-(aminomethyl)pyridine) and H_2dbcat, and it has been fully characterized including structure determination.

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