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1 **Bioinspired Mo, W and V complexes bearing a highly hydroxyl-functionalized** 2 **Schiff base ligand**

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9

10 **Abstract**

11 A series of bioinspired dioxidomolybdenum(VI), dioxidotungsten(VI) and oxidovanadium(V) complexes [MoO₂(H₂L^{Saltris})], [WO₂(H₂L^{Saltris})] and [VO(HL^{Saltris})]₂ were prepared
12 by the reaction of a hydroxyl-rich Schiff base proligand *N*-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-3,5-di-*tert*-butylsalicylaldimine (H₄L^{Saltris}) with metal
13 precursors in methanol solutions. Molybdenum and tungsten complexes crystallize as
14 mononuclear molecules, whereas the vanadium complex forms dinuclear units. From the
15 complexes, [VO(HL^{Saltris})]₂ shows activity in the oxidation of 4-*tert*-butylcatechol and 3,5-
16 di-*tert*-butylcatechol, mimicking the action of the dicopper enzyme catechol oxidase.*
17
18

19 **Introduction**

20 The easy exploitation of aerial dioxygen in the context of oxidation catalysis represents
21 one of the most desired goals in synthetic organic chemistry because of its ready
22 availability, low cost and environmental compatibility.[1] Nature has perfected the use of
23 the relatively inert dioxygen molecule in a wide variety of metabolic oxidation reactions
24 through metalloenzymes. Efforts to mimic various metalloenzyme active sites by
25 (bio)inorganic chemists can be divided into biomimetic (structural) and bioinspired
26 (functional) modelling.[2,3] A central idea in coordination chemistry is to use ligands
27 with diverse electronic and steric features to modulate the properties of central metals
28 in various model complexes, and thus achieve some properties related to natural enzyme
29 active sites.

30 The enzymes from the molybdenum oxotransferase superfamily catalyze oxygen atom
31 transfer (OAT) reactions, whereby an oxygen atom is transferred from a high-valent,
32 catalytically active (di)oxidomolybdenum species to a suitable donor/acceptor
33 molecule.[4,5] The superfamily can be divided into three subfamilies, namely xanthine
34 oxidase, sulfite oxidase and DMSO reductase.[6] The active sites of the eponymous
35 enzymes DMSO reductase and sulfite oxidase consist of a monooxido- and dioxidomolybdenum(VI) centers, respectively.[6] They, together with many other molybdoenzymes

List of abbreviations: 3,5-DTBC (3,5-di-*tert*-butylcatechol), 3,5-DTBSQ (3,5-di-*tert*-butylsemiquinone), 3,5-DTBQ (3,5-di-*tert*-butyl-1,2-benzoquinone), 4-TBC (4-*tert*-butylcatechol), 4-TBQ (4-*tert*-butyl-1,2-benzoquinone), OAT (oxygen atom transfer).

1 have been structurally and functionally modelled by a number of monooxido- and
2 dioxidomolybdenum(VI)- and tungsten(VI) complexes, which find applications in OAT
3 catalysis research.[7]

4 Vanadates and other vanadium-containing compounds have been studied for decades
5 due to their biological relevance and catalytic activity in a variety of oxidation
6 reactions.[8–11] Especially, the bioinorganic chemistry of vanadium, highlighted by the
7 three vanadium haloperoxidases and V-nitrogenase, as well as the anti-diabetic effects of
8 many vanadium compounds have motivated synthetic chemists to prepare model
9 compounds for use in oxidation catalysis, as well as in structural studies, and in medicinal
10 research.[12–14] Catechol oxidase is an dioxygen-activating dicopper enzyme[15–17]
11 which catalyzes the oxidation of catechols to the corresponding *o*-benzoquinones,
12 producing water as a by-product. A number of vanadium(IV) and vanadium(V) complexes
13 have also been discovered to efficiently catalyze the same reaction.[18–23]

14 Although compounds that display catechol oxidase mimetic activities are usually
15 reserved for of Cu coordination model compounds[24,25], recently many other metals
16 *e.g.* Co, Mn, Fe, Ni and Zn, as substitutes for copper, have also been used to reach moderate
17 to high conversions of various catechols to *o*-benzoquinones.[26–28] There are also some
18 examples on the catechol oxidase mimicking activity of molecular vanadium(IV) and
19 vanadium(V) complexes.[18–23] It is well established that various catechols readily form
20 redox non-innocent complexes with vanadium, where the vanadium center may be
21 assigned +III, +IV and +V oxidation states.[29–33] There are also some reports for
22 catecholate-containing molybdenum and even tungsten complexes.[34] In the case of
23 vanadium(V) complexation of catechols may lead to a reduction in the metal center (V(V)
24 → V(IV)), sometimes accompanied by cleavage of the oxido ligand.[30,31,33]

25 The mechanism(s) of vanadium-catalyzed oxidation of catechols are still not fully
26 understood. For example, many vanadium systems apparently demonstrate catechol
27 oxidase- and catechol dioxygenase-like activities simultaneously, leading to a number of
28 oxidation products ranging from intra- and extradiol cleavage products to autoxidation
29 products.[35,36] Furthermore, there is no definitive consensus on the nature of the active
30 catalyst, with some proponents in support of a “common catalyst hypothesis”, which
31 states that a specific vanadium-containing, catalytically active species is always formed
32 *in-situ* by vanadium-leaching regardless of used vanadium catalyst precursor.[36] This is
33 evidenced by very similar product distributions forming by the action of very different
34 precatalysts, as well as from indicative spectroscopic and spectrometric signatures.

35 In light of available data[37], the common catalyst has been suggested to be [VO(3,5-
36 DTBC)(3,5-DTBSQ)], which is formed during catalytic turnover conditions from its
37 catalytic resting-state [VO(3,5-DTBC)(3,5-DTBSQ)]₂, also known as Pierpont’s
38 complex.[29] The Pierpont’s complex itself is derived from H₂O₂-assisted leaching of
39 virtually any vanadium catalyst precursor, provided that 3,5-DTBC is present, in a so-
40 called autoxidation-product-initiated reaction pathway.[36,38] However, there are also
41 some reports of discrete oxidovanadium(V) catalysts where the supposed active catalyst,

1 allegedly not formed from metal leaching, has been identified using mass
2 spectrometry.[20,23]

3 Herein we describe the synthesis and characterization of dioxidomolybdenum(VI) and -
4 tungsten(VI) complexes (**1**, **2**) as well as the oxidovanadium(V) complex (**3**) and their
5 application as bioinspired synthetic analogues to molybdenum oxotransferases and
6 catechol oxidase. The syntheses of **1-3** involve complexation to a bulky Schiff base
7 proligand *N*-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-3,5-di-*tert*-butylsalicylal-
8 imine ($H_4L^{Saltris}$) featuring several alcohol side-arms. The presence of non-coordinating
9 hydrogen bond/donor acceptor moieties such as alcohols or amides in the outer
10 coordination spheres of various complexes has been associated with heightened catalytic
11 activities of the complexes in some oxidation reactions.[39,40] However, only **3** showed
12 catechol oxidase-like activities, forming 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DTBQ)
13 and 4-*tert*-butyl-1,2-benzoquinone (4-TBQ), respectively. Moreover, mechanistic studies
14 with regard to vanadium-catalyzed catechol oxidation were performed to further
15 elaborate on the nature of the active catalyst.

16 Experimental

17 All syntheses, experiments and manipulations were run in an ambient atmosphere.
18 $[MoO_2(acac)_2]$ (*acac* = acetylacetonato) and $[W(eg)_3]$ (*eg* = ethane-1,2-diolato = ethylene
19 glycolato) were prepared according to known methods.[41,42] Other reagents and
20 solvents were purchased from commercial sources and used as received. IR spectra were
21 recorded using a Bruker VERTEX 71 FTIR spectrophotometer equipped with a RT-
22 DLaDTGS detector. 64 scans were performed in the ATR mode for individual
23 measurements using a Harrick VideoMVP accessory. In this setup, the sample is pressed
24 against a diamond anvil. All data were recorded in transmittance mode with a resolution
25 of 4 cm^{-1} . The UV-Vis measurements were performed in MeOH, MeCN and $CHCl_3$ using a
26 \varnothing 1 cm quartz cuvette on an Agilent CARY60 spectrophotometer. High-resolution mass
27 spectra were recorded on a Bruker Daltonics MicroTOF-Q II electrospray ionization time-
28 of-flight (ESI-TOF) mass spectrometer using both negative and positive polarization as
29 well as in MSMS mode. Full UV-Vis, NMR, IR and ESI-MS spectra are given in the
30 supplementary material. The 1H , ^{13}C , ^{19}F and ^{51}V spectra were recorded on either Bruker
31 Avance III 600 MHz (1H : 600.16 MHz, ^{13}C : 150.91 MHz) equipped with a CryoProbe
32 Prodigy triple resonance inverse (TCI) probe or Bruker Avance 500 MHz (1H : 500.08 MHz
33 ^{13}C : 125.75 MHz, ^{19}F : 470.55 MHz, ^{51}V : 131.54 MHz) equipped with a broad-band observe
34 probe (Bruker BBO-5 mm-Zgrad). All 1H and ^{13}C NMR spectra are reported in ppm
35 downfield relative to tetramethylsilane (TMS, δ = 0.00 ppm) and referenced to residual
36 solvent signals $CHCl_3$ -H (1H : δ 7.26, ^{13}C : δ 77.16), DMSO-*H*₆ (1H : δ 2.50, ^{13}C : δ 39.52),
37 acetone-*H*₆ (1H : δ 2.05, ^{13}C : δ 206.26, 29.84) if TMS is not present.[43] The 0 ppm fluorine
38 and vanadium reference frequencies were calculated from the TMS 1H frequency using
39 the unified chemical shift scale by IUPAC ($E(^{19}F, CCl_3F)$ = 94.094011) and ($E(^{51}V, VOCl_3)$
40 = 26.302948), respectively.[44]

1 Syntheses

2 ***N*-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-3,5-di-*tert*-butylsalicylald-**
 3 **imine ($H_4L^{Saltris}$)**. The proligand was synthesized according to a published procedure
 4 with slight modifications.[28] Detailed synthetic procedure is disclosed in the ESI. Yield:
 5 3.08 g (91 %). 1H NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 14.90 (1H, d, J = 2.2 Hz, ArOH),
 6 8.55 (1H, d, J = 2.2 Hz, Ar—CH=N—CR₃), 7.27 (1H, d, J = 2.5 Hz, ArH), 7.22 (1H, d, J = 2.5
 7 Hz, ArH), 4.70 (3H, t, J = 5.4 Hz, NC—(CH₂OH)₃), 3.62 (6H, d, J = 5.4 Hz, NC—(CH₂OH)₃),
 8 1.37 (9H, s, *t*-Bu), 1.27 (9H, s, *t*-Bu). ^{13}C NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 165.37,
 9 160.21, 138.12, 136.18, 126.57, 125.98, 117.49, 66.80, 61.41, 34.55, 33.78, 31.32, 29.29.
 10 IR/cm⁻¹ ATR mode: ν 3500–3000vb (ROH, ArOH, R(CH₂OH)₃), 2958–2868s (C—H, *t*-Bu),
 11 1620s (RCH=N), 1593–1361m (arom. C=C), 1252m (C—O, ArOH), 1049vs, 1038vs (C—
 12 O, R(CH₂OH)₃), 882m, 644s.

13 **[MoO₂(H₂L^{Saltris})], 1.** 337 mg (1.0 mmol) H₄L^{Saltris} and 326 mg (1.0 mmol) [MoO₂(acac)₂]
 14 were dissolved in 15 mL MeOH in a 50 mL Erlenmeyer flask equipped with a magnetic
 15 stir-bar. The clear yellow reaction mixture was stirred at RT for 72 hours, after which it
 16 was transferred to a -25 °C freezer. In a week, single crystals suitable for XRD had formed
 17 and were subsequently isolated by Büchner filtration, washed with small amounts of ice-
 18 cold MeOH, and air-dried to afford the analytically pure target complex. Yield: 340 mg (73
 19 %). 1H NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 8.49 (1H, s, Ar—CH=N—CR₃), 7.47 (1H,
 20 d, J = 2.5 Hz, ArH), 7.44 (1H, d, J = 2.5 Hz, ArH), 4.95 (2H, t, J = 5.5 Hz, NRC—(CH₂OH)₂),
 21 4.43 (2H, s, NR₂C—(CH₂O⁻)), 3.73 (2H, dd, J_1 = 11.3 Hz, J_2 = 5.5 Hz, NRC—(CH₂OH)₂), 3.63
 22 (2H, dd, J_1 = 11.3 Hz, J_2 = 5.5 Hz, NRC—(CH₂OH)₂), 1.37 (9H, s, *t*-Bu), 1.29 (9H, s, *t*-Bu).
 23 ^{13}C NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 164.72, 156.92, 140.49, 137.92, 129.20,
 24 128.55, 120.60, 76.65, 73.69, 61.28, 48.61, 34.89, 33.97, 31.27, 29.62. IR/cm⁻¹ ATR mode:
 25 ν 3500–3000vb (ROH, R(CH₂OH)₂), 2956–2866s (C—H, *t*-Bu), 1620s (RCH=N), 1562–
 26 1361m (arom. C=C), 1038vs (C—O, R(CH₂OH)₃), 1253m (C—O, ArOH), 1045s (C—O,
 27 R(CH₂OH)₂ and R(CH₂O⁻)), 916vs ν_s (MoO₂)[45–48] 880vs ν_{as} (MoO₂)[45–48], 761m, 558s
 28 ν (Mo—N)[49]. UV-Vis (MeCN; λ_{max} / nm (ϵ / M⁻¹ cm⁻¹) 355 (3180). ESI-HRMS⁺ [M+Na]⁺
 29 calculated m/z = 488.0945, found m/z = 488.0900. ESI-HRMS⁻ [M-H]⁻ calculated m/z =
 30 464.0980, found m/z = 464.1056.

31 **1** could be also synthesized using equimolar amounts of H₄L^{Saltris} and Na₂MoO₄ · 2 H₂O.
 32 However, excess glacial acetic acid was required, as well as overnight refluxing. Yield
 33 using this methodology was also slightly reduced (277 mg, 60 %).

34 **[WO₂(H₂L^{Saltris})], 2.** 337 mg (1.0 mmol) H₄L^{Saltris} and 330 mg (1.0 mmol) Na₂WO₄ · 2 H₂O
 35 were dissolved in 15 mL MeOH in a 100 mL Erlenmeyer flask equipped with a magnetic
 36 stir-bar. The solution was treated with 1 mL glacial acetic acid, heated to boil in an oil-
 37 bath for two hours, then left to stir for 72 hours at RT. The pale reaction mixture was
 38 concentrated to *ca.* half of the original volume, filtered and transferred to +5 °C
 39 refrigerator. Upon *ca.* two weeks of storage, pale yellow microcrystals suitable for single
 40 crystal XRD had deposited. They were subsequently isolated by Büchner filtration,
 41 washed with small amounts of ice-cold MeOH and air-dried to afford the analytically pure

1 target compound. Yield: 258 mg (47 %). ^1H NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 8.46
 2 (1H, s, Ar—CH=N—CR₃), 7.53 (1H, d, *J* = 2.4 Hz, ArH), 7.47 (1H, d, *J* = 2.4 Hz, ArH), 4.99
 3 (2H, t, *J* = 5.4 Hz, NRC—(CH₂OH)₂), 4.58 (2H, s, NR₂C—(CH₂O⁻)), 3.72 (2H, dd, *J*₁ = 11.1
 4 Hz, *J*₂ = 3.4 Hz, NRC—(CH₂OH)₂), 3.63 (2H, dd, *J*₁ = 11.1 Hz, *J*₂ = 3.4 Hz, NRC—(CH₂OH)₂),
 5 1.38 (9H, s, *t*-Bu), 1.30 (9H, s, *t*-Bu). ^{13}C NMR (DMSO-*d*₆, 298 K, 600 MHz, TMS) δ 165.51,
 6 155.81, 141.03, 138.36, 129.37, 129.06, 121.22, 76.76, 73.72, 61.17, 48.61, 34.85, 33.97,
 7 31.26, 29.60. IR/cm⁻¹ ATR mode: ν 3500–3000_{vb} (ROH, R(CH₂OH)₂), 2958–2850_s (C–H,
 8 *t*-Bu), 1621_s (RCH=N), 1566–1362_m (arom. C=C), 1300_m (C—O, ArOH), 1048_{vs} (C—O,
 9 R(CH₂OH)₂ and R(CH₂O⁻)), 893_{vs} ν_s (WO₂)[45–48] 860_{vs} ν_{as} (WO₂)[45–48], 764_m, 561_s
 10 ν (W—N)[49]. UV-Vis (MeOH; λ_{max} / nm (ϵ / M⁻¹ cm⁻¹) 365 (2440). ESI-HRMS⁺ [M+Na]⁺
 11 calculated *m/z* = 574.1399, found *m/z* = 574.1435. ESI-HRMS⁻ [M-H]⁻ calculated *m/z* =
 12 550.1424, found *m/z* = 550.2204.

13 **2** could be also synthesized using equimolar amounts of H₄L^{Saltris} and [W(eg)₃]. The
 14 isolated yield of a 1 mmol scale synthesis was very low, only 40 mg (9 %).

15 **[VO(HL^{Saltris})₂, 3**. 337 mg (1.0 mmol) H₄L^{Saltris} and 265 mg (1.0 mmol) [VO(acac)₂] were
 16 dissolved in 15 mL MeOH in a 100 mL Erlenmeyer flask equipped with a magnetic stir-
 17 bar. Upon *ca.* 15 minutes of stirring at RT, an umber-colored solid precipitated out of
 18 solution. The solid was collected by Büchner filtration, washed with *ca.* 30 mL RT MeOH,
 19 and air-dried to afford the target compound in a pure non-crystalline form. UMBER-
 20 colored single crystals suitable for x-ray diffraction were obtained from hot acetonitrile
 21 solution upon slow cooling. Yield: 357 mg (89 %). ^1H NMR (acetone-*d*₆, 298 K, 600 MHz,
 22 TMS) δ 9.08 (1H, s, Ar—CH=N—CR₃), 7.66 (1H, d, *J* = 2.5 Hz, ArH), 7.53 (1H, d, *J* = 2.5 Hz,
 23 ArH), 5.25 (1H, d, *J* = 14.3 Hz, NR₂C—(CH_AH_BO⁻)_A), 5.13 (2H, m, NR₂C—(CH_AH_BO⁻)_A and
 24 NR₂C—(CH_AH_BO⁻)_B), 4.70 (1H, d, *J* = 8.9 Hz, NR₂C—(CH_AH_BO⁻)_B), 4.58 (1H, t, *J* = 5.4 Hz,
 25 NR₂C—(CH₂OH)_C), 4.04 (2H, dd, *J*₁ = 5.6 Hz, *J*₂ = 3.2 Hz, NR₂C—(CH₂OH)_C), 1.51 (9H, s, *t*-
 26 Bu), 1.35 (9H, s, *t*-Bu). ^{13}C NMR (acetone-*d*₆, 298 K, 600 MHz, TMS) δ 165.46, 160.98,
 27 141.26, 137.84, 131.29, 129.74, 121.38, 85.88, 81.87, 79.65, 64.51, 35.99, 34.84, 31.70,
 28 30.45. ^{51}V NMR (acetone-*d*₆, 298 K, 600 MHz, VOCl₃) δ -562. IR/cm⁻¹ ATR mode: ν 3571_w
 29 (ROH), 2954–2864_s (C–H, *t*-Bu), 1623_s (RCH=N), 1556–1360_m (arom. C=C), 1303_m (C—
 30 O, ArOH), 1075_s, 1030_s (C—O, R(CH₂OH)₂ and R(CH₂O⁻)), 893_{vs} ν (V=O)[19,22,50].
 31 853_m, 764_m, 552_s. UV-Vis (MeCN; λ_{max} / nm (ϵ / M⁻¹ cm⁻¹) 520 (550). ESI-HRMS⁺ [M+Na]⁺
 32 calculated *m/z* = 825.2718, found *m/z* = 825.2599. ESI-HRMS⁻ [M + Cl]⁻ calculated *m/z* =
 33 837.2508, found *m/z* = 837.2273.

34 **3** could be also synthesized using equimolar amounts of H₄L^{Saltris} and VOSO₄ · 5 H₂O, with
 35 two equivalents of Et₃N added as a base. Similarly to the synthesis involving [VO(acac)₂],
 36 an umber solid was quickly precipitated out of solution, however, with a slightly lowered
 37 yield; a 1.0 mmol scale synthesis yielded 277 mg of the target compound, corresponding
 38 to a yield of 69 %.

39

1 X-ray crystallography

2 Single crystal X-ray data were collected using Rigaku Oxford diffraction SuperNova
3 diffractometer equipped with micro-focus single-source (Mo-K α radiation, $\lambda = 0.71073$
4 Å) and Eos detector. Data collection and processing were done using CrysAlis^{Pro}[51]
5 software. Crystal structures were solved and refined within Olex²[52] GUI using
6 SHELXS[52] and SHELXL[53] programs, respectively. Atoms heavier than H were located
7 from the difference density map and refined anisotropically. All C—H atoms were
8 calculated to their ideal positions and refined using a riding model with the isotropic
9 displacement parameters fixed to values corresponding to 1.2–1.5 times the U_{aniso} of the
10 respective host atom. O—H hydrogen atoms that participate in hydrogen bond
11 interactions were located from the difference density map and refined isotropically
12 without restrictions in displacement parameters. The single crystal X-ray data for **1–3** are
13 given in ESI table S1. Crystallographic data for the compounds reported in this paper
14 were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road,
15 Cambridge CB21EZ, UK. These data can be obtained free of charge on quoting the
16 depository number CCDC 1959437–1959439 (E-Mail: deposit@ccdc.cam.ac.uk,
17 <http://www.ccdc.cam.ac.uk>). The powder x-ray diffraction measurements were
18 performed using a Huber G670 detector (Cu-K α radiation, $\lambda = 1.5406$ Å). For each
19 individual measurement, the exposure time was set to 30 min and with a total of 10 scans.

20 Cyclic voltammetry

21 The cyclic voltammetry electrochemical measurements of **1–3** ($c = 1 \times 10^{-3}$ M) were
22 performed using a standard three-electrode setup using an Autolab PGSTAT101
23 potentiostat. The CVs were recorded at RT using \varnothing 1 mm platinum and glassy carbon (GC)
24 working electrodes. Before use both working electrodes were polished using 6, 3, 1 and
25 0.25 μm diamond paste, and rinsed with quartz distilled water and technical ethanol. The
26 quasi-reference electrode was an Ag/AgCl wire, and it was calibrated against the
27 ferrocene redox-couple (Fc/Fc⁺) ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.55$ V).[54] A coiled platinum wire was
28 employed as the counter electrode. Measurements were performed using 50, 100 and
29 200 mV s^{-1} scanning rates in dry electrochemical grade acetonitrile with 0.1 M tetrabutyl-
30 ammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. Prior to every
31 measurement, the sample solutions were bubbled with dry N₂ for 10 minutes. The
32 electrochemical window was $-2.5 - 2.5$ V for GC working electrode, and $-0.8 - 2.3$ V for
33 Pt electrode, respectively.

34 Oxygen atom transfer reactions

35 All complexes were preliminarily assessed in the formal oxygen atom transfer (OAT)
36 reactions of tris(4-fluorophenyl)phosphine (P(*p*-C₆H₄F)₃) to the corresponding tris(4-
37 fluorophenyl)phosphine oxide (P(*p*-C₆H₄F)₃O).[55] In the OAT experiments, 500 μL of 5
38 $\times 10^{-3}$ M P(*p*-C₆H₄F)₃ in DMSO-H₆ solution and 500 μL of 5×10^{-4} M **1–3** in DMSO-H₆
39 solution were combined in a screw-capped scintillation vial and maintained for 24 hours
40 at 60 °C in a thermal oven. Additionally, a control reaction involving 1000 μL 5×10^{-3} M

1 P(*p*-C₆H₄F)₃ in DMSO-H₆ solution was also run. In all cases, the conversion was assessed
 2 by ¹⁹F NMR and after the 24-hour period. All measurements were run in duplicate and
 3 the results obtained are given as the average of the two reactions.

4 **Oxidation of 4-TBC and 3,5-DTBC**

5 The oxidations of 4-TBC and 3,5-DTBC to 4-TBQ and 3,5-DTBQ were monitored by *in-situ*
 6 UV-Vis spectroscopy on an Agilent Cary 60 UV-Vis spectrophotometer and a Ø 1.00 cm
 7 quartz cuvette. All measurements were run in duplicate and conducted at room
 8 temperature (25 °C) under ambient atmosphere. The reaction kinetics were assessed
 9 using the method of initial rates. For this, a 1.00 × 10⁻⁵ M solution of precatalyst **3** was
 10 prepared in CHCl₃. The substrate concentration was varied 1000, 2000, 3000, 4000, 6000,
 11 8000 and 10000-fold relative to the catalyst to evaluate the substrate dependence of the
 12 reactions for 4-TBC. In the case of 3,5-DTBC, substrate concentration ratios of 12500,
 13 15000 and 17500 were additionally used. The reactions were initiated directly in the
 14 quartz cuvette by combining 1.500 mL precatalyst solutions and 1.500 mL of 1.75 × 10⁻¹
 15 M – 1.00 × 10⁻² M substrate solutions. Accordingly, final concentrations of [cat] = 5.00 ×
 16 10⁻⁶ M and [S] = 8.75 × 10⁻² M – 5.00 × 10⁻³ M, respectively, were obtained during
 17 catalysis. The progress of the reaction was monitored by following the increase in the
 18 absorbance at *ca.* 388 nm due to 4-TBQ and 3,5-DTBC (ε(4-TBQ) = 1150 M⁻¹ cm⁻¹ and
 19 ε(3,5-DTBQ) = 2200 M⁻¹ cm⁻¹)[56,57] for 10 minutes at every one-minute interval.
 20 Absorbance vs. time graphs were plotted, and initial reaction rates at every concentration
 21 were determined directly utilizing the on-board Cary WinUV Kinetics software. Finally,
 22 the initial reaction rates and the substrate concentrations were fitted, using Origin 2015
 23 software, to the Michaelis–Menten equation (1) using non-linear regression analysis, in
 24 order to obtain the maximum reaction rate *V*_{max}, Michaelis constant *K*_M ([S] at ½*V*_{max}) and
 25 turnover frequency *k*_{cat} values. The turnover frequency was calculated using the formula
 26 (2), where [*E*_T] is the catalyst concentration.

$$27 \quad v = \frac{V_{\max} \times [S]}{K_M + [S]} \quad (1)$$

$$28 \quad k_{\text{cat}} = \frac{V_{\max}}{[E_T]} \quad (2)$$

29 **Iodometric assay**

30 Hydrogen peroxide was determined from the catechol oxidation reaction mixture based
 31 on I₃⁻, which has a characteristic UV-Vis absorbance at *ca.* 353 nm in water. A 100 mL
 32 Erlenmeyer flask was charged with *ca.* 1 g 4-*tert*-butylcatechol and dissolved in 30 mL
 33 CHCl₃. 1 mol-%, or *ca.* 48 mg **3** was added to the reaction mixture, which was
 34 subsequently stirred for several days at RT. Afterwards, the reaction mixture was
 35 extracted with 25 mL distilled water. The aqueous phase was adjusted to a pH ~ 2 with
 36 dilute aqueous H₂SO₄, and a portion of it was treated with *ca.* 0.32 M KI (aq) solution and
 37 was allowed to react overnight. I₃⁻ was observed by UV-Vis spectroscopy at *ca.* 353 nm,
 38 whereas no such signal was observed for the bare KI solution, which was allowed to react

1 with atmospheric oxygen overnight. Additionally, to further confirm the presence of
2 hydrogen peroxide, a portion of the KI solution was treated with excess amounts of 30 %
3 aqueous H₂O₂, and the formation of a 353 nm band was again observed (ESI Figure S57)

4 **Mechanistic catechol oxidation investigations**

5 The UV-Vis spectroscopic investigations were performed in 1 cm quartz cuvettes by
6 combining 1.500 mL 0.100 M 4-TBC chloroform solution containing 0.010 M BHT, DMSO
7 or H₂O₂, and 1.500 mL chloroform solutions consisting of 1×10^{-4} M **3**. For H₂O₂ tests,
8 0.020 and 0.030 M solutions were additionally used. For control reactions, 0.100 M 4-TBC
9 reacts with 0.030 M H₂O₂ in the absence of **3** (control 1), and 0.100 M 4-TBC reacts with
10 1×10^{-4} M **3** in the absence of H₂O₂ (control 2). The initial reaction rates were determined
11 using the on-board Cary WinUV Kinetics software as described above. All measurements
12 were repeated once, and the results given in figure 7 represent average values obtained
13 from the two measurements.

14 For ⁵¹V NMR and ESI-HRMS studies, 6 mg of **3** was suspended in 650 μL CDCl₃ and treated
15 with 100 equivalents of 3,5-DTBC (166 mg) or 4-TBC (124 mg) to reflect the
16 stoichiometry of the kinetic catechol oxidation experiments. Prior to measurements the
17 solutions were filtered through a small cotton plug to remove any undissolved solids. ⁵¹V
18 NMR measurements were performed immediately after filtration. The same CDCl₃
19 solutions were diluted in MS grade acetonitrile, and subsequently analyzed by ESI-HRMS
20 immediately after the ⁵¹V NMR measurements.

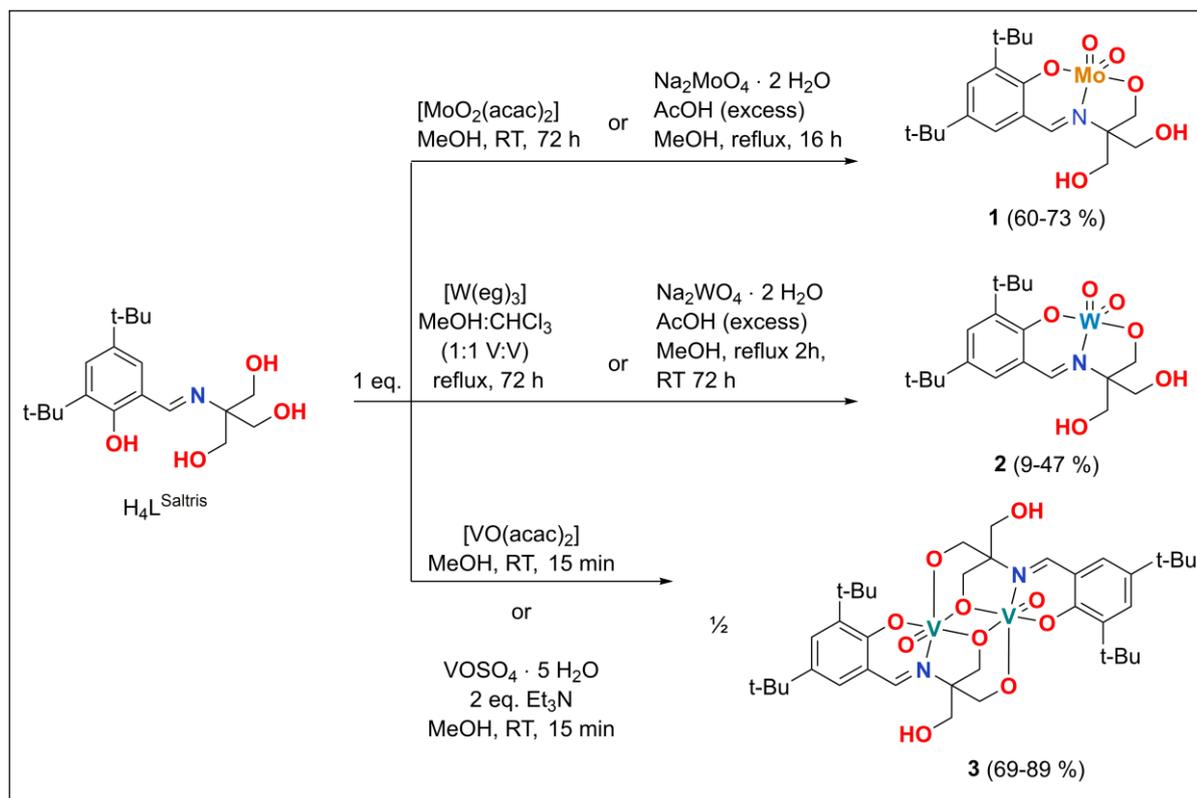
21 To determine the product distribution in the oxidation of 3,5-DTBC, 500 mg of 3,5-DTBC
22 and 18 mg of **3** (1 mol-%) were allowed to react in 30 mL boiling chloroform under
23 ambient atmosphere overnight for *ca.* 16 hours in a 50 mL round-bottomed flask
24 equipped with a magnetic stir-bar and a reflux condenser. Afterwards, the reaction
25 mixture was analyzed by TLC on silica plates with technical DCM. Three components with
26 R_f-values *ca.* 0.85, 0.58 and 0.33 were detected. The compounds were isolated by column
27 chromatography on silica gel (technical DCM), and identified with ¹H, ¹³C NMR and
28 positive mode ESI-HRMS according to published data (ESI).[35]

29 **Results and discussion**

30 **Syntheses and characterization of complexes**

31 The ligand precursor H₄L^{Saltris} was synthesized according to a slightly modified
32 procedure.[28] We were also interested in the corresponding H₅L^{Saltris} amine analogue,
33 but our attempts to obtain it through reductive amination from H₄L^{Saltris} proved
34 unsuccessful. However, Mannich reaction did provide the target compound, although
35 unselectively, and with trace yields only. Accordingly, complexations were not tested
36 with H₅L^{Saltris}. The Mannich reaction including the product distribution is presented the
37 electronic supplementary information (Scheme S1). The spectral data of all products are
38 also listed in the ESI.

1 H_4L^{Saltris} reacts with equimolar amounts of molybdenum precursors $[MoO_2(acac)_2]$ or
 2 $Na_2MoO_4 \cdot 2 H_2O$ in methanol to afford *cis*- $[MoO_2(H_2L^{\text{Saltris}})]$ (**1**) as a yellow crystalline
 3 solid, whereas the use of $[MoO_2(acac)_2]$ provides slightly better yields. Likewise, the
 4 tungsten precursor $[W(eg)_3][42]$ gave *cis*- $[WO_2(H_2L^{\text{Saltris}})]$ (**2**) in methanol as pale
 5 crystals, although the (isolated) yield was very low. However, $Na_2WO_4 \cdot 2 H_2O$ can be used
 6 to obtain **2** in a moderate yield. Vanadium precursor $[VO(acac)_2]$ rapidly reacts with
 7 H_4L^{Saltris} in methanol at RT to form an umber-colored precipitate in a high yield. The solid
 8 can be crystallized from hot acetonitrile to yield analytically pure **3** with a formula
 9 $[VO(HL^{\text{Saltris}})]_2$. The schematic representation of the complex syntheses is given in scheme
 10 1.



12 All complexes were fully characterized by means of high-resolution electrospray
 13 ionization time-of-flight mass spectrometry in positive and negative ionization modes,
 14 also utilizing MSMS. Characteristic to all complexes in the positive ionization mode is the
 15 presence of multiple singly charged sodium adducts of the type $[M - nH + (n+1)Na]^+$,
 16 where $n = 1, 2, 3$. In these species the protons in the trisbase alcohol arms of the
 17 complexes are sequentially substituted by sodium ions. However, singly protonated
 18 adducts of the type $[M + H]^+$ are generally not observed. Other common adducts in the
 19 positive ionization are singly charged oligomerized adducts of general type $[nM+Na]^+$,
 20 where $n = 1, 2, 3$. These are most likely formed by electrostatic interactions, and not
 21 representative of genuine species observable outside ionizing conditions. In the negative
 22 ionization mode, the most characteristic ionization adduct is the $[M-H]^-$ from the loss of
 23 a proton. Other common adducts are chlorido adducts of the type $[M+Cl]^-$, and
 24 dealkylation adducts $[M-R]^-$, where R represent a generic alkyl or alcohol group.

1 Similarly to what is observed in the positive ionization mode, electrostatic
2 oligomerization is evident in the negative mode also.

3 The UV-Vis spectra of $H_4L^{Saltris}$, **1**, **2** and to a certain extent **3**, are rather similar, and
4 contain three clear electronic absorptions. All UV-Vis spectra are presented in ESI figure
5 14, and the spectral data has been tabulated in Table 1. By comparing the UV-Vis
6 spectrum of $H_4L^{Saltris}$ to those of **1–3** it may be concluded that all signals below *ca.* 400 nm
7 in the case of **1** and **2**, or below *ca.* 460 nm in the case of **3** are primarily of intraligand
8 origin. While all electronic absorptions in the proligand are visible in the UV-Vis spectra
9 of the complexes, a noticeable redshift is observed in all signals, consistent with
10 coordination. All high-intensity ($\epsilon \geq 2000\text{--}20000\text{ M}^{-1}\text{ cm}^{-1}$) electronic absorptions below
11 *ca.* 240 nm, and the second, lower energy ($\epsilon \sim 1150\text{--}17700\text{ M}^{-1}\text{ cm}^{-1}$) absorptions at *ca.*
12 260–287 nm in all compounds are attributed to $\pi \rightarrow \pi^*$ transitions in the aromatic ring
13 and due to extended conjugation in the salicylaldimine chromophore. The third band at
14 *ca.* 328–363 for $H_4L^{Saltris}$, **1** and **2** is assigned to the $n \rightarrow \pi^*$ transitions ($\epsilon \sim 40\text{--}3200\text{ M}^{-1}$
15 cm^{-1}) in the aldimine functionality.[58] **3** also contains this transition, however, it is
16 eclipsed by what are clearly multiple overlapping absorptions in the general area
17 between *ca.* 320–460 nm. These multiple signals have been assigned as LMCT transitions,
18 most likely attributable to alkoxido to vanadium(V) transitions.[59] A very low-intensity
19 LMCT at *ca.* 520 nm is assigned to phenolato \rightarrow V(V) ($p_\pi \rightarrow d$), with an $\epsilon \sim 550\text{ M}^{-1}\text{ cm}^{-1}$.
20 [59] The $p_\pi \rightarrow d$ transitions in **1** and **2**, although they must exist, are too weak to be
21 appropriately assigned. Likewise, the alkoxido to metal LMCT bands are much weaker in
22 **1** and **2** compared to **3**.

23 In the IR spectra of all compounds, a broad signal at 3100–3500 corresponds to the
24 phenolic and/or alcoholic OH groups while a strong stretching vibration of the imine
25 group occurs at around 1622 cm^{-1} . The complexation of Mo, W and V to $H_4L^{Saltris}$ can be
26 substantiated from corresponding metal oxido stretching vibrations.[29] Specifically, the
27 characteristic symmetric and asymmetric $\nu(MO_2)$ ($M = Mo, W$) stretches are found at 930
28 and 889 cm^{-1} for **1**, and at 946 and 893 cm^{-1} for **2**, respectively.[47] These are in line
29 with what has been reported for similar dioxidomolybdenum complexes.[60] For **3**,
30 featuring only a single oxido ligand, a characteristic $\nu(V=O)$ stretching vibration is found
31 at 952 cm^{-1} , which is consistent with experimental values obtained for other
32 oxidovanadium(V) complexes bearing similar ligands.[49,59] Furthermore, a low energy
33 signal at 553 cm^{-1} can be seen, which is assigned as $\nu(V-N)$ stretch.[61] This signal is
34 also found in **1** at 557 cm^{-1} and is tentatively assigned to $\nu(Mo-N)$, since similar
35 stretching vibrations are known in dioxidomolybdenum(VI) complexes bearing variable
36 bidentate cysteamine-type ligands.[62] The signal seen in the IR spectrum of **2** at 562 cm^{-1}
37 is cautiously assigned to $\nu(W-N)$ stretches by virtue of similarity to **1**. It should be
38 emphasized, that the strong signal in question is missing in the IR spectrum of the
39 proligand. IR spectral data for the most characteristic signals in all compounds in
40 presented in table 1.

41

1

Table 1. IR and UV-Vis data for H₄L^{Saltris} and **1–3**. See text for further information

Compound	IR (cm ⁻¹)				
	$\nu(\text{O—H})$	$\nu(\text{C=N})$	$\nu(\text{M=O})$	$\nu_{\text{asymm.}}(\text{M=O})$	$\nu(\text{M—N})$
H ₄ L ^{Saltris}	3100–3500	1622	–	–	–
1	3100–3500	1620	930	889	557
2	3100–3500	1621	946	893	562
3	3570	1623	952	–	553
Compound	UV-Vis				
	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	transition		
H ₄ L ^{Saltris}	225	≥ 2000	$\pi \rightarrow \pi^*$		
	262	1150	$\pi \rightarrow \pi^*$		
	328	400	$n \rightarrow \pi^*$		
1	230	≥ 20000	$\pi \rightarrow \pi^*$		
	260	16700	$\pi \rightarrow \pi^*$		
	355	3200	$n \rightarrow \pi^*$		
2	230	≥ 20000	$\pi \rightarrow \pi^*$		
	274	12500	$\pi \rightarrow \pi^*$		
	363	2500	$n \rightarrow \pi^*$		
3	240	≥ 20000	$\pi \rightarrow \pi^*$		
	287	17700	$\pi \rightarrow \pi^*$		
	320–460	~ 7600 –700	$n \rightarrow \pi^*$		
	520	550	$p\pi \rightarrow d$		

2

3 For H₄L^{Saltris} the reported ¹H NMR data[28] significantly differs from that obtained by us,
4 possibly due to the some difficulties in the measurements in the previous report. In any
5 case, the ¹H and ¹³C NMR data obtained by us are in good agreement with the expected
6 structure of the ligand precursor and as such, we find re-publication of good NMR data
7 warranted. Striking features in the ¹H NMR spectrum of H₄L^{Saltris}, very useful for structure
8 determination, are the proton signals corresponding to the phenol, aldimine carbon, and
9 tris-alcohol sidearms. The ¹H NMR data for H₄L^{Saltris} and **1–3** is given in table 2.

10 The signal for the phenolic proton is found at 14.90 ppm, which is significantly downfield
11 for what would generally be expected for phenols or salicylaldehydes, at around 10 ppm
12 or below. Schiff bases derived from salicylaldehydes are known to exist as tautomers,
13 shifting between their enolimine (OH) and ketoenamine (NH) forms, through what is
14 known as RAHB (resonance assisted intramolecular hydrogen bonding).[63,64] The
15 significant downfield resonance for the phenol proton in H₄L^{Saltris} can be attributed to
16 moderate de-shielding effect caused by the intramolecular hydrogen bonding to the
17 aldimine nitrogen (ArO—H---N=R¹R²).[64,65] Furthermore, with similar molecules the
18 ¹³C chemical shift of the *ipso* carbon atom connected to phenol OH is known to be sensitive
19 to the relative tautomeric population between OH and NH forms, with lower average
20 values of *ca.* 155 ppm, and higher average values of *ca.* 180 ppm generally being expected
21 for OH, and NH forms, respectively.[64,65] In H₄L^{Saltris} the corresponding ¹³C NMR signal
22 is found at 160.21 ppm in DMSO-*d*₆, indicative of tautomeric equilibrium favoring the OH

1 form, a feature that is also common for similar compounds.[64] A small J-coupling (2.2
2 Hz) between the phenol-apparent and aldimine carbon proton can be seen in the ^1H NMR
3 spectrum in DMSO-*d*₆. In light of tautomeric equilibrium, this coupling has been shown
4 to arise from $^3\text{J}_{\text{NH},\alpha\text{H}}$ vicinal coupling between NH and CH of the ketoenamine form.[64]
5 Small J-couplings of this type have been encountered before for similar compounds.[64]
6 Other information, particularly useful for determining coordination mode of $\text{H}_4\text{L}^{\text{Saltris}}$ to
7 various metals, are the proton signals of the tris-alcohol sidearms. In $\text{H}_4\text{L}^{\text{Saltris}}$ the three
8 alcohol protons are clearly visible at δ 4.70, as a triplet, with a $^3\text{J}_{\text{HH}} = 5.4$ Hz coupled to the
9 six vicinal methylene protons, appearing as a duplet, at δ 3.62 ($^3\text{J}_{\text{HH}} = 5.4$ Hz) when
10 relatively dry DMSO-*d*₆ is used.

11 The coordination mode of $\text{H}_4\text{L}^{\text{Saltris}}$ to Mo, W and V was unequivocally determined by NMR
12 in addition to single-crystal XRD. Quite unsurprisingly, the corresponding *cis*-
13 dioxidomolybdenum(VI) and -tungsten(VI) complexes *cis*- $[\text{MO}_2(\text{H}_2\text{L}^{\text{Saltris}})]$, where M = Mo
14 or W, share analogous structures in DMSO solution as well. $\text{H}_4\text{L}^{\text{Saltris}}$, as a potentially
15 pentadentate ligand, coordinates to both metal centers in tridentate, dianionic manner
16 *via* the phenolato oxygen, aldimino nitrogen and one alcoholato sidearm.[66,67] The
17 coordination mode is clearly evident from ^1H NMR in dry DMSO-*d*₆. For example, the
18 phenol proton at δ 14.90 is missing, and the aromatic protons have been shifted
19 downfield, relative to $\text{H}_4\text{L}^{\text{Saltris}}$, for *ca.* 0.21 ppm and 0.26 ppm for **1** and **2**, respectively.
20 Curiously, the signal corresponding to aldimine CH proton is shifted upfield very slightly
21 (< 0.10 ppm) in both complexes relative to $\text{H}_4\text{L}^{\text{Saltris}}$. These effects might be explained by
22 inductive effects: Upon coordination of the aldimine nitrogen, its electron density is
23 withdrawn towards the electron-deficient Mo(VI) and W(VI) centers, manifesting as a
24 slight shielding effect for the aldimine CH proton.

25 As was disclosed earlier, the three alcohol protons in $\text{H}_4\text{L}^{\text{Saltris}}$ are clearly visible as a
26 triplet, however, in the complexes these same triplets only correspond to two protons. In
27 **1**, the triplet corresponding to two free sidearm alcohol protons is found slightly
28 downfield relative to $\text{H}_4\text{L}^{\text{Saltris}}$ at δ 4.95 ppm, ($^3\text{J}_{\text{HH}} = 5.5$ Hz), whereas in **2** it is located at δ
29 4.99 ppm. In both complexes, the four methylene protons corresponding to the two
30 uncoordinated alcohol sidearms appear as duplets of duplets, at δ 3.73 and 3.64 for **1**, and
31 δ 3.72 and 3.63 ppm for **2**, respectively. Accordingly, the methylene CH₂ for the
32 coordinated alcoholato sidearm is found, as a singlet, at δ 4.43 for **1** and δ 3.58 for **2**.

33 The most distinguishable feature of the ^{13}C NMR spectra for **1** and **2** relative to that of
34 $\text{H}_4\text{L}^{\text{Saltris}}$ are the methylene CH₂ carbons in the alcohol sidearms. In **1** and **2** these become
35 inequivalent due to expected slightly different electronic environments and steric
36 perturbations caused by coordination to the metals. Except for the quaternary carbon
37 connecting to the alcoholato arms and aldimino nitrogen, which is upshifted in both
38 complexes for *ca.* 18 ppm, the alcohol and alcoholato methylene protons have been
39 downshifted for *ca.* 15 ppm in both **1** and **2**, consistent with coordination and changes in
40 electronic environment.

Table 2. ^1H NMR spectral data of $\text{H}_4\text{L}^{\text{Saltris}}$, **1–3** (δ in ppm). Multiplicity: s = singlet, d = duplet, t = triplet, m = multiplet (unresolved), b = broad.

Compound	ArOH	CH=N	Arom. H	NC(CH ₂ OH) ₃	NC(CH ₂ OH) ₃	tBu
$\text{H}_4\text{L}^{\text{Saltris}}$	14.90 (d, 1H)	8.55 (d, 1H)	7.27, 7.22 (d, 1H)	4.70 (t, 3H)	3.61 (d, 6H)	1.37, 1.27 (s, 9H)
1	-	8.49 (s, 1H)	7.47, 7.44 (d, 1H)	4.95 (t, 2H)	3.73; 3.64 (dd, 2H); (dd, 2H)	1.37, 1.29 (s, 9H)
2	-	8.46 (s, 1H)	7.53, 7.47 (d, 1H)	4.99 (bt, 2H)	3.72; 3.64 (dd, 2H); (dd, 2H)	1.38, 1.30 (s, 9H)
3	-	9.08 (s, 1H)	7.66, 7.53 (d, 1H)	4.58 (t, 1H)	5.25 (d, 1H) 5.13 (m, 2H) 4.70 (d, 1H) 4.04 (dd, 2H)	1.51, 1.35 (s, 9H)

1

2 In the oxidovanadium(v) complex **3**, $\text{H}_4\text{L}^{\text{Saltris}}$ coordinates in a tetradentate, trianionic
3 fashion *via* phenolato, aldimino and two alcoholato groups, in stark contrast to **1** and **2**.
4 In principle, ^1H NMR spectrum of **3** agrees well with a trigonal bipyramidal coordination
5 mode, which is common for vanadium(v) complexes. In the absence of single crystal XRD
6 and ^{51}V NMR measurements, comparable 5-coordinate solution-state structure has also
7 been proposed for several very similar vanadium(v) complexes.[59] However, in our
8 case, single crystal XRD reveals that **3** is dinuclear in the solid state (see discussion
9 below), with both vanadium centers adopting a distorted octahedral coordination mode.
10 Furthermore, ^{51}V NMR shows only one signal, which supports the dinuclear configuration
11 in solution state as well, since both vanadium centers are chemically equivalent.
12 Generally speaking, 5-coordinate vanadium complexes may isomerize to 6-coordinate
13 species *via*, for example, solvent ligand exchange, and vice versa. Furthermore, 6-
14 coordinate vanadium complexes may have multiple isomers if a solvent molecule is
15 coordinated. These dynamics are frequently observed as multiple signals in the ^{51}V NMR,
16 although the choice of NMR solvent may or may not greatly influence this. The single ^{51}V
17 NMR signal supports the notion that **3** is 6-coordinate, and is rigid *i.e.* does not contain
18 any coordinated solvent molecules in the solution state.

19 In **3**, the aldimine carbon proton and aromatic protons have been moderately shifted
20 downfield for *ca.* 0.34 and 0.27 ppm, respectively, relative to $\text{H}_4\text{L}^{\text{Saltris}}$. Similarly to **1** and
21 **2**, where the tris-alcohol sidearms become inequivalent relative to the free ligand, in **3**
22 these changes are much more pronounced. For example, the methylene CH₂ protons for
23 the two alcoholato sidearms, have been shifted downfield by 0.79 – 1.35 ppm. They also
24 appear separately as diastereotopic duplets, due to formation of rigid 5- and 6-membered
25 ring structures, respectively. The single free alcohol sidearm, on the other hand, appears
26 0.59 ppm downshifted for OH, and 0.13 ppm for the CH₂ protons, respectively.

27 The ^{13}C NMR spectrum of **3** is very similar to those of **1** and **2**. Most striking features are
28 the collapse of the equivalent (in $\text{H}_4\text{L}^{\text{Saltris}}$) tris-alcohol carbons to inequivalent carbons in
29 **3**, with approx. 15 ppm shift downfield observed for the two coordinating alcoholato
30 methylene protons. Strikingly, the ^{51}V NMR spectrum of **3** shows only one signal at *ca.* –
31 562 ppm. The simple nature of the ^{51}V NMR spectrum points towards that **3** is present, in
32 solution, as a one stable species, and that there is probably little if any solution dynamics

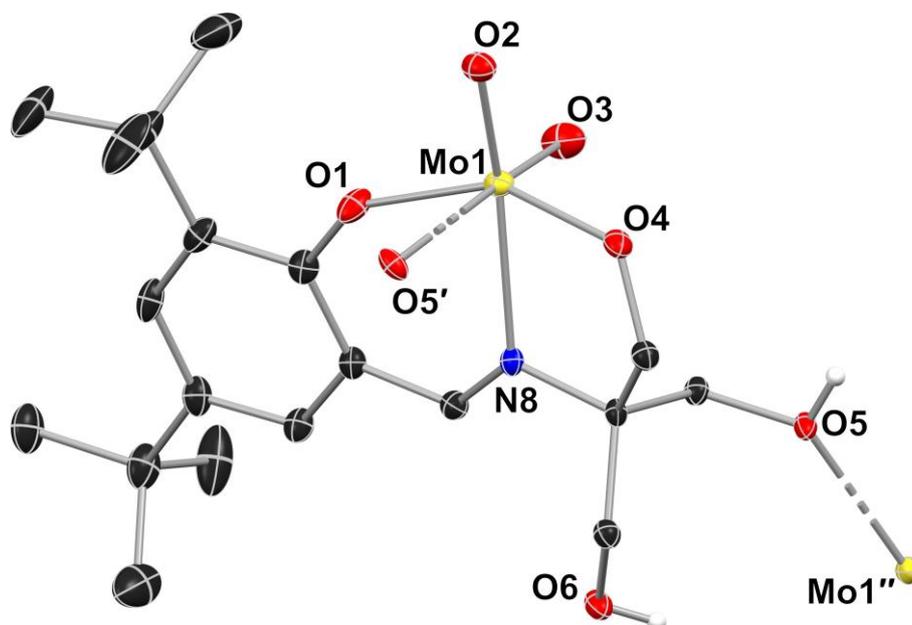
1 commonly encountered with vanadium compounds. The ^{51}V NMR observation is well in
 2 line with single-crystal XRD results, in that the complex unit is symmetric, and both
 3 oxidovanadium(v) centers adopt rigid six-coordinate distorted octahedral
 4 configurations, making the vanadium centers chemically equivalent. The obtained ^{51}V
 5 NMR spectrum is closely similar to those of other related oxidovanadium(v)
 6 complexes.[49] Furthermore, the ^{51}V NMR signal is present in the expected general area[†]
 7 attributable to oxidovanadium systems bearing redox-innocent O_4N type ligands.[33,68]

8 Description of crystal and molecular structures

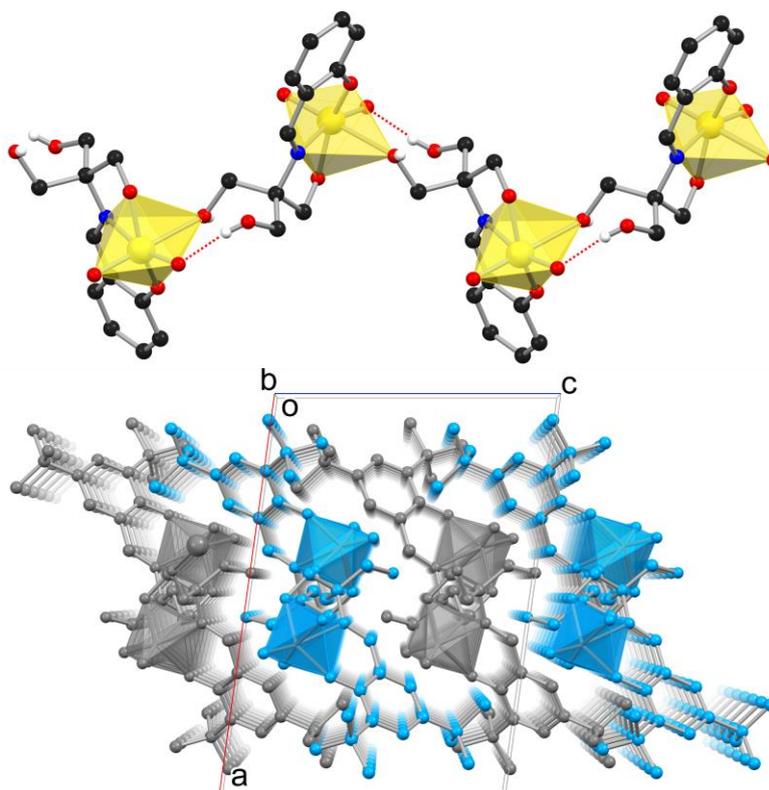
9 Good quality single crystals of **1–3** could be grown thus enabling their structural
 10 characterization by single crystal X-ray diffraction methods. **1** and **2** crystallized directly
 11 from the reaction mixtures, *i.e.* from methanol as brightly yellow needle-like crystals (**1**)
 12 and pale yellow needle-like crystals (**2**). **3**, on the other hand, deposited from the
 13 methanol reaction mixture in a non-crystalline form. Umber-colored block-like crystals
 14 could be obtained from boiling acetonitrile upon slow cooling. All three complexes
 15 crystallize in the monoclinic crystal system and have the same space group ($P2_1/c$).

16 The X-ray structure of **1** (Figures 1 and 2) reveals that the reaction between molybdenum
 17 precursor and $\text{H}_4\text{L}^{\text{Saltris}}$ has involved the deprotonation of two proligand OH groups – the
 18 phenolic and one of the three alcoholic OH moieties – and coordination of the respective
 19 O atoms to the dioxidomolybdenum(vi) center. The rather distorted octahedral
 20 coordination sphere of the Mo(vi) ion is fulfilled by the aldimino N donor and one of the
 21 alcoholic OH groups of an adjacent complex unit (for selected bond parameters, see
 22 Figure 1). A CSD survey[69] of dioxidomolybdenum(vi) complexes with similar trisbase
 23 salicylaldimine-type ligands reveals that in such complexes only one of the three available
 24 alcoholic groups tends to coordinate to the central metal ion, similarly to **1**. Furthermore,
 25 the remaining sixth coordination site in the previously reported complexes is occupied
 26 by a solvent molecule (H_2O , MeOH, DMF or DMSO), which leads to discrete molecular
 27 complexes. In the crystal structure of **1**, however, the distinguishable complex units
 28 couple together via $\text{Mo}—\text{O}_{\text{alcohol}}$ bonds thus creating a polymeric 1D chain along the
 29 crystallographic *b*-axis. The polymeric system is further stabilized by intrapolymer
 30 $\text{Mo}=\text{O}\cdots\text{H}—\text{O}$ [$d(\text{O}2\cdots\text{O}6') = 2.65 \text{ \AA}$] hydrogen bonds (HB) as well as interpolymer HBs
 31 occurring *via* $\text{Mo}—\text{OH}\cdots\text{OHCH}_2\text{CN}$ [$d(\text{O}5'\cdots\text{O}6'') = 2.63 \text{ \AA}$] contacts. It is noteworthy that,
 32 albeit being polymeric in the solid state, **1** dissolves readily in DMSO which can be
 33 attributed to the degradation of the polymeric chains into the respective monomeric
 34 complex units (see NMR analysis above). This confirms the lability of the $\text{Mo}—\text{O}_{\text{alcohol}}$
 35 bonds and the discrete nature of the complex upon dissolution.

[†] V(v) complexes bearing a redox-innocent O_5N_1 donor set generally appear between *ca.* –600 to –400 ppm according to ref. [33] and at lowest *ca.* –650 ppm according to ref. [68] (δ ppm vs. VOCl_3).

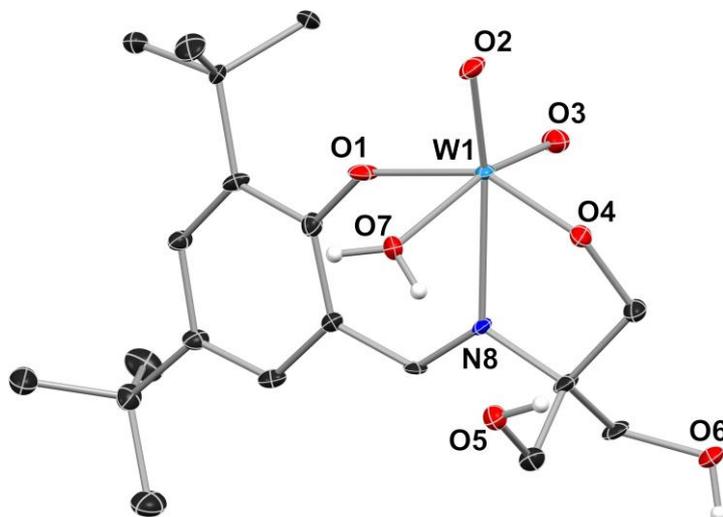


1 **Figure 1.** Presentation of the asymmetric unit of **1** with bonds to the neighboring complex
 2 units shown in dashed lines. All C—H hydrogen atoms are omitted for clarity. Principal
 3 ellipsoids are presented at the 50 % probability level. Relevant bond lengths (Å): Mo1—
 4 O1 = 1.9300(14), Mo1—O2 = 1.7237(12), Mo1—O3 = 1.6942(13), Mo1—O4 =
 5 1.9060(13), Mo1—O5' = 2.4123(13) and Mo1—N8 = 2.2912(14). Symmetry operations:
 6 (') = 1-x, ½+y, ½-z; (') = 1-x, -½+y, ½-z.



7 **Figure 2.** Partial view of the 1D polymeric structure of **1** (top) and illustration of packing
 8 of the discrete polymers (alternating blue and grey colors, below) viewed along the
 9 crystallographic *b*-axis. Top: C—H hydrogen atoms and *tert*-butyl groups omitted. Below:
 10 All hydrogen atoms omitted.

1 In contrast to **1**, the respective tungsten analogue **2** crystallizes as monomeric units in
 2 which the WO_2 unit is bound to a dianionic tridentate $\text{H}_2\text{L}^{\text{Saltris}}$ ligand in agreement with
 3 the NMR analyses. The remaining coordination site, which is *trans* to O3, has been taken
 4 up by a water molecule (Figure 3). Although there is one example of tungsten complex
 5 bearing a very similar ligand, the $[\text{WO}_2(\text{sapd})]$ (sapd = salicylidene propanediol)[70], to
 6 the best of our knowledge, **2** is the first report of a tungsten complex characterized by
 7 XRD that bears a Saltris-type Schiff base ligand. It should be noted, that the solid state
 8 structure of **2** closely resembles some known Mo-complexes[‡] such bearing Saltris-like
 9 ligands.[58,71] In **2**, two of the three ligand alcoholic OH groups remain uncoordinated
 10 and are thus available for hydrogen bonding. In case of **2**, this leads to an intricate
 11 hydrogen bonding network in the crystal lattice in which the monomeric units build into
 12 2D sheets, terminated by the aliphatic regions of the molecules (ESI, Figure S59).

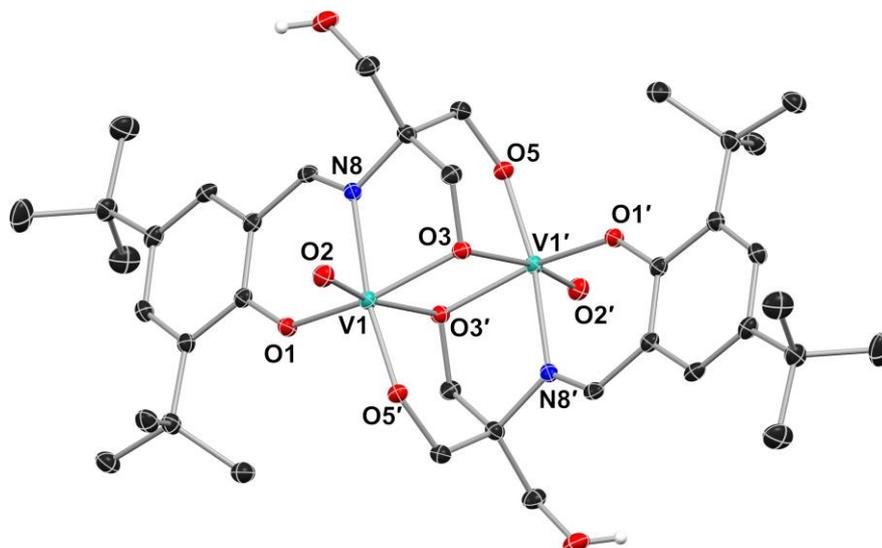


13 **Figure 3.** Illustration of the asymmetric unit of structure of **2**. All C—H hydrogen atoms
 14 are omitted for clarity. Principal ellipsoids are presented at the 50 % probability level.
 15 Relevant bond lengths (Å): W1—O1 = 1.928(4), W1—O2 = 1.764(4), W1—O3 = 1.715(4),
 16 W1—O4 = 1.902(4), W1—O7 = 2.309(4) and W1—N8 = 2.283(4).

17 X-ray structure of **3** shows a formation of a dinuclear vanadium complex consisting of
 18 two oxidovanadium(v) centers and two ligands wherein each ligand is coordinated in
 19 tetradentate trianionic fashion (Figure 4). The crystal structure is solved with half of the
 20 $[\text{VO}(\text{HL}^{\text{Saltris}})]_2$ dimer constituting the asymmetric unit while the complete
 21 centrosymmetric complex is generated via an inversion center between the V atoms. Also,
 22 an acetonitrile solvent molecule is located in the asymmetric unit. The crystallo-
 23 graphically unique complex moiety comprises of oxidovanadium(v) ion chelated in ONO
 24 fashion by phenolato (O1), aldimino (N8) and alcoholato (O3) groups of $\text{HL}^{\text{Saltris}}$. The
 25 dimer is upheld by alcoholato atoms O3 and O3', which act as bridging donors between
 26 the V(v) centers, and alcoholato atoms O5 and O5' which coordinate to neighboring V1'
 27 and V1, respectively. This bonding scheme yields an approximately planar (maximum
 28 deviation from planarity is ca. 17°) V_2O_6 system to which two alcoholato and two
 29 aldimino groups coordinate perpendicularly. The V—O distances in the V1—O3/O3'—

[‡] Solid state structure of **2** is very similar to MoO_2 complexes **1–5** from ref. [58] and **1–3** from ref. [71].

1 V1' bridges show high degree of asymmetry (ca. 0.4 Å). Structurally, **3** is very similar to
 2 some other reported dimeric vanadium complexes bearing analogous ligands.[49,66,72]



3 **Figure 4.** Presentation of the $[VO(HL^{\text{Saltris}})]_2$ complex found in the crystal structure of **3**.
 4 All C—H hydrogen atoms are omitted for clarity. Principal ellipsoids are presented at
 5 the 50 % probability level. Relevant bond lengths (Å): V1—O1 = 1.8646(12), V1—O2 =
 6 1.6009(13), V1—O3 = 1.9028(12), V1—O3' = 2.3066(12), V1—O5' = 1.7981(12) and
 7 V1—N8 = 2.1323(15). Symmetry operations: (') = -x, 1-y, 1-z.

8 X-ray powder diffraction analysis

9 Bulk samples of **1–3** were analyzed by powder X-ray diffraction (PXRD). The unit cell
 10 parameters of complexes **2** and **3** were determined by Pawley analysis[73] within the
 11 HighScore Plus 4.7 program using the cell parameters of corresponding single crystal
 12 structures as the starting point of the least-squares refinements. The variable parameters
 13 in the refinements were zero-offset, unit cell and peak profile parameters. The fitted
 14 diffraction graphs for **2** and **3** are found in ESI figures S61–62 whereas the refined unit
 15 cells and the resulting R-factors and goodness-of-fit values are presented in ESI table S2.
 16 For **2**, due to instrument limitations, we could not record one of the major low angle peaks
 17 which resides at ca. 4.5° according to the simulated single crystal pattern.

18 In case of complex **1**, the experimental PXRD pattern shows some similarities with the
 19 pattern simulated from the respective single crystal structure but it is in general
 20 distinctively different (ESI figure S60). We suspect that this may arise from a degradation
 21 of the polymeric structure of **1** while preparing the sample of PXRD analysis by grinding
 22 of the crystalline bulk material. In contrast, the unit cell parameters of bulk materials of
 23 **2** and **3**, derived from the Pawley analysis, are in good agreement with the corresponding
 24 single crystal structures and thus demonstrate their structural similarity. The refined
 25 unit cells (PXRD) show ca. 2 % increase in unit cell volume which is reasonable
 26 considering the thermal expansion due to the differences in data recording temperature
 27 between the single crystal and powder data (120 vs. 298 K)

1 Cyclic voltammetry

2 To gain insight into the reactivity of the complexes, and specifically to study the ability of
 3 **1–3** to undergo reversible redox-reactions relevant regarding catechol oxidation,
 4 electrochemical investigations were undertaken. The cyclic voltammograms of **1–3** are
 5 presented in the electronic supplementary material, while the electrochemical data has
 6 been tabulated in table 3. **3** has a reversible electrochemical response with $E_{1/2} = -415$ mV
 7 with Pt working electrode, and $E_{1/2} = -422$ mV using GC working electrode, respectively.
 8 This response has been assigned as the V(v)/V(iv) redox-couple, since it is also observed
 9 in the same potential area with some other structurally similar[§] Schiff base
 10 oxidovanadium(v) complexes.[49,59]. With higher scan rates, slight quasi-reversibility is
 11 observed, although $E_{1/2}$ does not change significantly. In the positive potential range three
 12 irreversible oxidation responses occur at $E_{1/2} = ca. +900$ mV, +1.496 and +1.683 V (Pt WE),
 13 that are most likely ligand-centered, since they are also varyingly present in **1** and **2**. For
 14 example, in some unrelated complexes phenoxyl radical formation has been suggested to
 15 occur at approx. +650–750 mV.[74] Accordingly, we tentatively assign the $\sim +900$ mV
 16 redox-response to $PhO \rightarrow PhO^{\bullet+}$, and subsequent oxidation events at higher potentials to
 17 alkoxy-centered oxidations *i.e.* $RO \rightarrow RO^{\bullet+}$. The cyclic voltammograms of **1** and **2** are
 18 remarkably featureless in comparison to those of **3**. All redox-processes present in **1** and
 19 **2** are irreversible, with the one-electron reductions *e.g.* Mo(VI) \rightarrow Mo(V) and W(VI) \rightarrow
 20 W(V) tentatively assigned as -0.896 (Pt) and -1.296 V (GC), respectively.[66] Similar
 21 ligand-centered irreversible oxidation events are present in **1** and **2** than what is found
 22 in **3**.

Table 3. Electrochemistry data obtained for **1–3**.

Complex	ligand-centered <i>e.g.</i> $RO \rightarrow RO^{\bullet+}$		ligand-centered <i>e.g.</i> $RO \rightarrow RO^{\bullet+}$		ligand-centered <i>e.g.</i> $PhO \rightarrow PhO^{\bullet+}$		metal-centered $M(ox)/M(ox+1)$	
	Pt	GC	Pt	GC	Pt	GC	Pt	GC
1	–	+2.159	+1.691	+1.717	–	+0.942	–	–0.986 irrev.
2	–	–	+1.653	+1.684	+0.934	+0.959	–	–1.296 irrev.
3	+1.683	1.682	+1.496	+1.484	+0.896	+0.917	–0.415 ps. rev.	–0.422 ps. rev.

The values are given in V vs. Ag/AgCl calibrated against Fc/Fc⁺ redox-couple.[54] GC and Pt represent glassy carbon and platinum working-electrodes (WE), respectively.

23

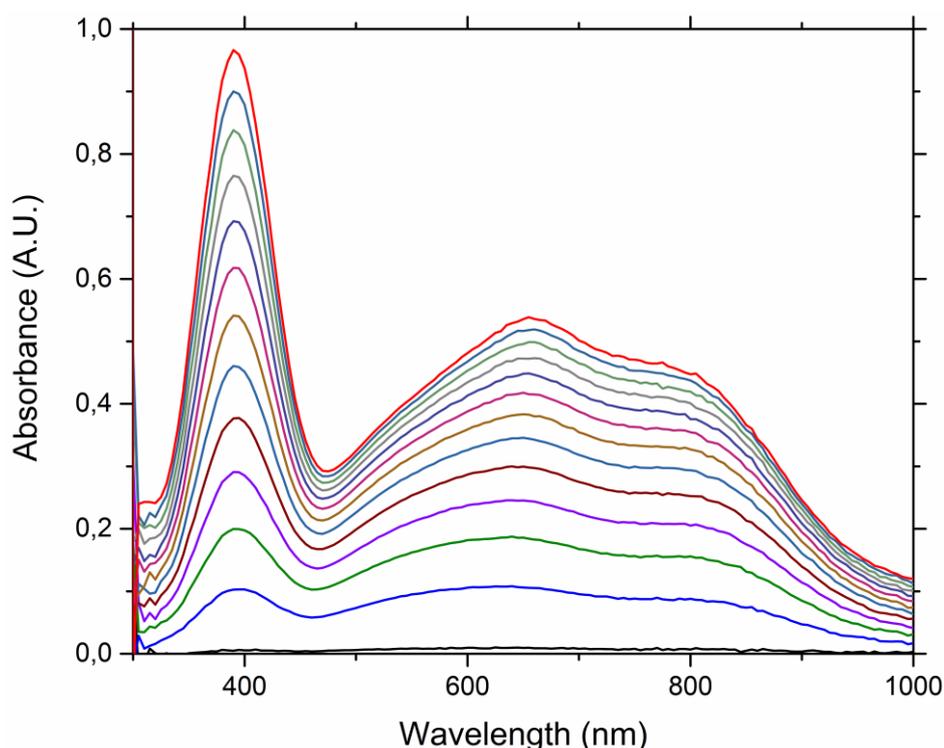
24 Catechol oxidase mimetic activity

25 In various catechol oxidase studies 3,5-DTBC is the substrate of choice[19,20,28], owing
 26 to its relatively easy oxidation due to its low redox potential.[75] As such, the catechol
 27 oxidase mimetic activity of all complexes was studied in the aerial oxidation of 3,5-DTBC
 28 as well as 4-*tert*-butylcatechol (4-TBC) and pyrocatechol in chloroform, acetonitrile and

[§] Structurally related V(v) complexes such as **3** and **6–8** from ref [49] and **1, 2, 4** and **5** from ref. [59] display a V(iv)/V(v) redox couple at $E_{1/2}$ values -470 to -400 mV vs. Ag/AgCl in DMF.

1 methanol. 4-TBC and pyrocatechol were chosen because they are more resistant to
2 autoxidation compared to 3,5-DTBC.

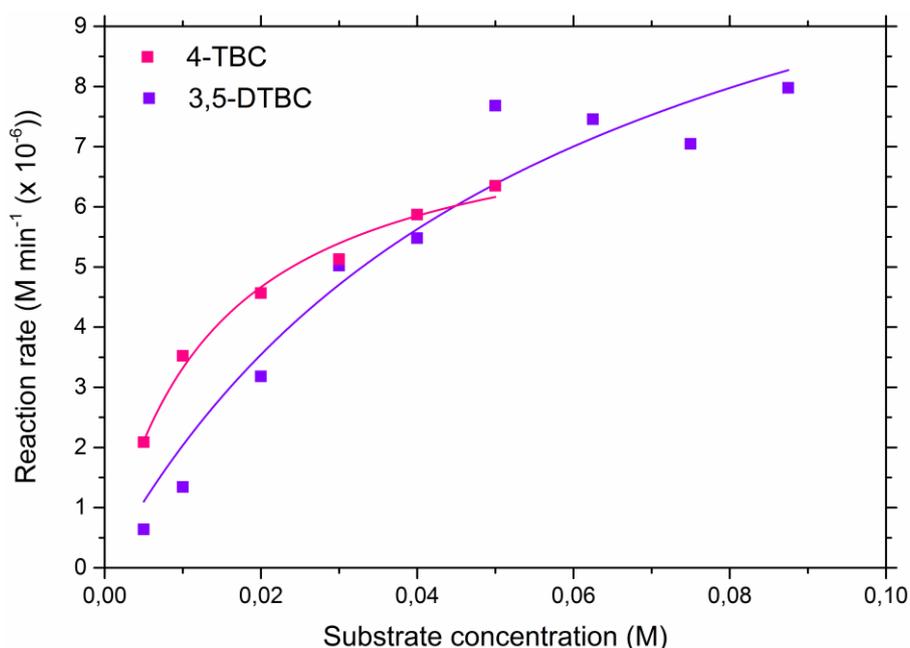
3 Preliminary investigations indicated that 3,5-DTBC and 4-TBC readily reacted to form the
4 corresponding *o*-benzoquinones, namely 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DTBQ)
5 and 4-*tert*-butyl-1,2-benzoquinone (4-TBQ), respectively, when **3** was used as the
6 catalyst in CHCl₃, MeOH and MeCN. However, **1** and **2** showed no noticeable catechol
7 oxidase-like activity in the same time frame, although UV-Vis and ESI-HRMS
8 measurements confirmed that the catechols coordinate to the metal centers (ESI Figures
9 S35–S46). Furthermore, pyrocatechol was observed not to react in any solvent with any
10 of the catalysts. With **3**, catechol coordination was also evident from the fact that all of
11 the reaction solutions turned blue after the addition of the catechols, a characteristic
12 color for vanadium-catecholato species[31], with also typical vanadium-catecholato
13 LMCT bands observable in the UV-Vis spectra at *ca.* 650 and 830 nm (figure 5).[31,33,76]
14 Furthermore, the solutions eventually turned green and finally yellow-brown due to the
15 formation of *o*-benzoquinones. UV-Vis spectroscopic measurements confirmed the UV
16 bands of 3,5-DTBQ and 4-TBQ, that appear at approx. 400 nm.[56,57]



17 **Figure 5.** The formation characteristic vanadium-catecholato LMCT bands at approx. 650
18 and 830 nm during 3,5-DTBC oxidation by **3**. The reaction was monitored for 1 hour and
19 spectra were recorded at every 5-minute interval.

20 From the kinetics data it can be concluded that the oxidation of 4-TBC and 3,5-DTBC
21 catalyzed by **3** follows typical Michaelis–Menten like kinetics (figure 6). At low substrate
22 concentrations, the measured absorbance increases linearly as a function of time,
23 indicative of a first order reaction with respect to the substrate. However, upon
24 significant excess (> 10 000-fold) of the substrate relative to catalyst the reaction rate

1 becomes pseudo zero-order. At this regime subsequent substrate additions will not speed
 2 up the reaction, as the catalyst becomes saturated. The kinetic parameters V_{\max}
 3 (maximum reaction rate), Michaelis-constant K_M ($[S]$ at $\frac{1}{2}V_{\max}$) and k_{cat} (turnover
 4 frequency) are given in table 4. From the kinetics data it can be seen that **3** compares well
 5 with other oxidovanadium systems, with its catalytic activity falling well within the range
 6 of that of others (table 4).[18–21] However, the most remarkable aspect is the fact that **3**
 7 offers a comparable catechol oxidase-like activity to the structurally very similar dicobalt
 8 complex $[\text{Co}(\text{H}_2\text{L}^{\text{Saltris}})(\text{OAc})]_2$. [28]



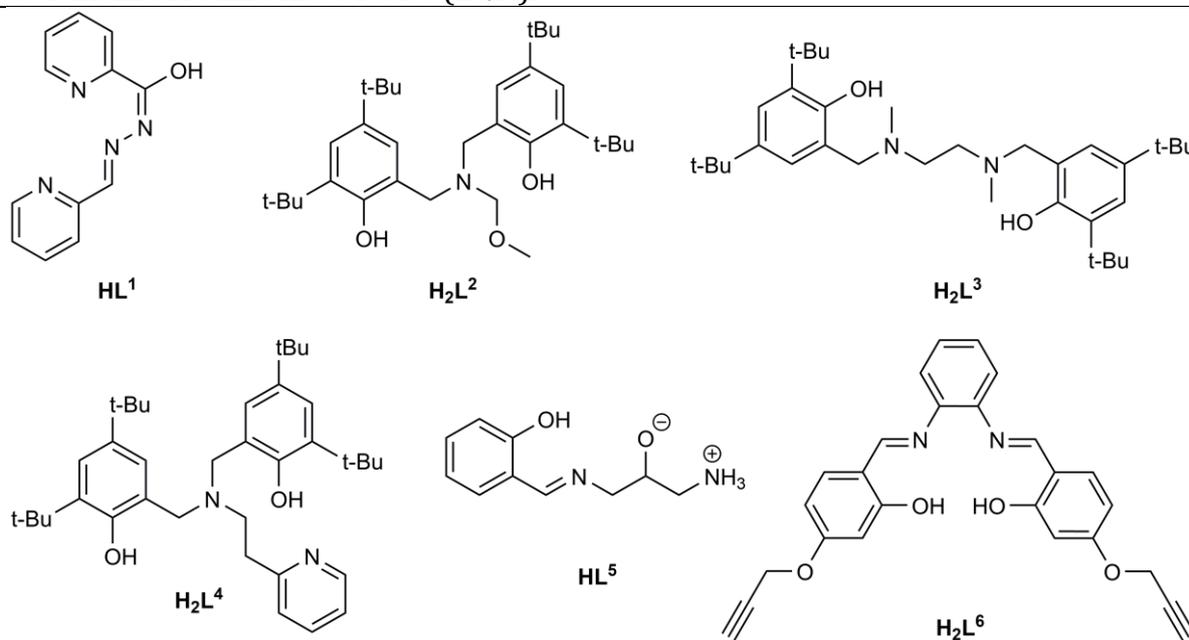
9 **Figure 6.** Michaelis–Menten plots of the oxidations of 4-TBC and 3,5-DTBC by **3** in CHCl_3 .

10 While the natural catechol oxidase catalyzes the oxidation of catechols to corresponding
 11 *o*-benzoquinones, producing water[15] as the sole by-product, a number of model
 12 transition metal complexes produce hydrogen peroxide as well.[28,77–81] Recently, a
 13 dicobalt complex $[\text{Co}(\text{H}_2\text{L}^{\text{Saltris}})(\text{OAc})]_2$ structurally strikingly similar (lacking oxido
 14 ligands) to **3** was assessed in the oxidation of 3,5-DTBC.[28] Mechanistic investigations
 15 involving MS measurements strongly hint towards a single and double 3,5-DTBSQ
 16 adducts $[(\text{Co}(\text{III})(\text{HL}^{\text{Saltris}})\text{Co}(\text{II})(\text{H}_2\text{L}^{\text{Saltris}})(3,5\text{-DTBSQ})]$ and $[\text{Co}(\text{II})(\text{H}_2\text{L}^{\text{Saltris}})(3,5\text{-}$
 17 $\text{DTBSQ})]_2$. Some studies highlight the importance of metal–metal distance, which may
 18 give insights into the overall catalytic mechanisms of any given catechol oxidase model
 19 system.[78,79] In light of the obvious structural similarities between the dinuclear
 20 cobalt(III) complex and our dinuclear oxidovanadium(v) complex, as well as the fact that
 21 there are only a limited[20,23] mechanistic investigations on catechol oxidation involving
 22 modern oxidovanadium systems, we conducted mechanistic investigations of our own
 23 using UV-Vis, ^{51}V NMR and ESI-HRMS spectrometry. The detailed descriptions of the
 24 experiments are given in supplementary material.

Table 4. Catechol oxidation results for the present $[\text{VO}(\text{HL}^{\text{Saltris}})]_2$ as well as some other selected vanadium-based catechol oxidase mimetic systems.

Compound	k_{cat} (h^{-1})	K_{M} (M)	V_{max} (M min^{-1})	Ref.
3	164 \pm 32 ^a	0.05727	1.37×10^{-5}	This work
3	94 \pm 4 ^b	0.01363	7.84×10^{-6}	This work
$[\text{VO}(\text{L}^1)]_2 \text{SO}_4$	1439 ^{bc}	–	–	[18]
$[\text{VO}(\text{OMe})(\text{L}^2)]$	12 ^a	0.00115	1.01×10^{-5}	[21]
$[\text{VO}(\text{OMe})(\text{L}^3)]$	13 ^a	0.00107	1.04×10^{-5}	[21]
$[\text{VO}(\text{OMe})(\text{MeOH})(\text{L}^4)]$	3 ^a	0.00557	7.66×10^{-6}	[19]
$[\text{Co}(\text{H}_2\text{L}^{\text{Saltris}})(\text{OAc})_2$	80 ^a	0.0087	1.33×10^{-5}	[28]
$[\text{VO}_2(\text{L}^5)]$	2063 ^a	0.00079	5.73×10^{-5}	[20]
$[\text{VO}(\text{L}^6)]$	395 ^a	0.00103	6.58×10^{-3}	[23]

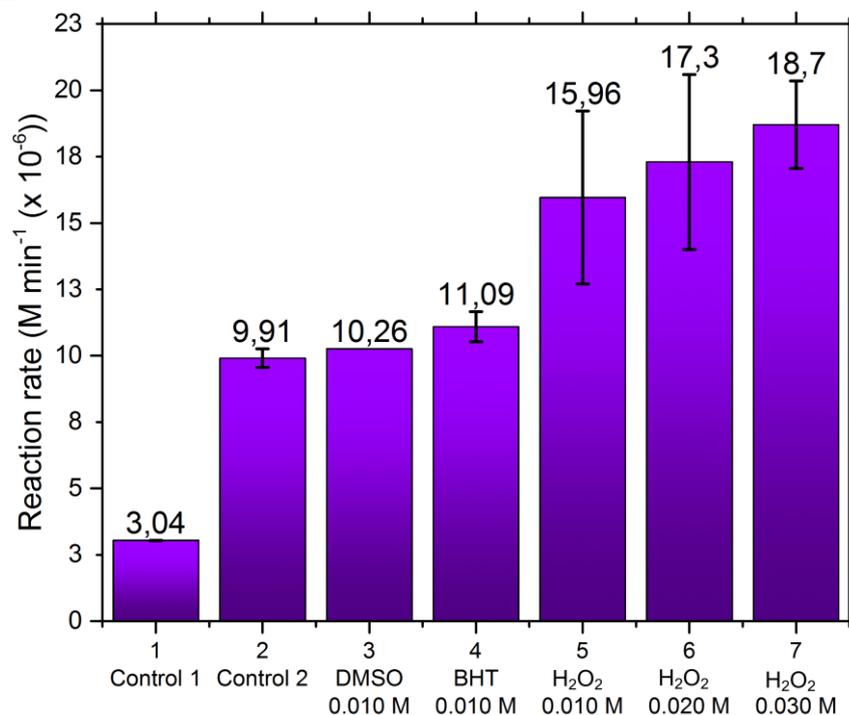
^a = For oxidation of 3,5-DTBC. ^b = For oxidation of 4-TBC. ^c = In the presence of stoichiometric amounts of base (Et_3N).



1

2 The initial reaction rate of the oxidation of 4-TBC by 0.1 mol-% of **3** was measured by UV-
3 Vis spectroscopy in the presence of DMSO (hydroxyl radical quencher), BHT (butyrated
4 hydroxytoluene, radical inhibitor), and varying concentrations of H_2O_2 in chloroform
5 (figure 7). The addition of DMSO or BHT (entries 3 and 4) have little effect on the initial
6 reaction rate when compared to the effects of **3** alone (entry 2), so it may be concluded
7 that hydroxyl radicals or any other radicals most likely do not significantly contribute to
8 the overall oxidation mechanism. However, hydrogen peroxide seems to accelerate the
9 oxidation to some extent in the presence of **3**, with reaction rate increasing approx.
10 linearly with increasing H_2O_2 concentration (entries 5–7). However, and importantly,
11 even in relatively high concentrations H_2O_2 does not significantly oxidize 4-TBC in the
12 absence of **3** (entry 1), so the reaction rate enhancement most probably does not come
13 from the direct substrate oxidation by H_2O_2 . Indeed, it has been previously shown that

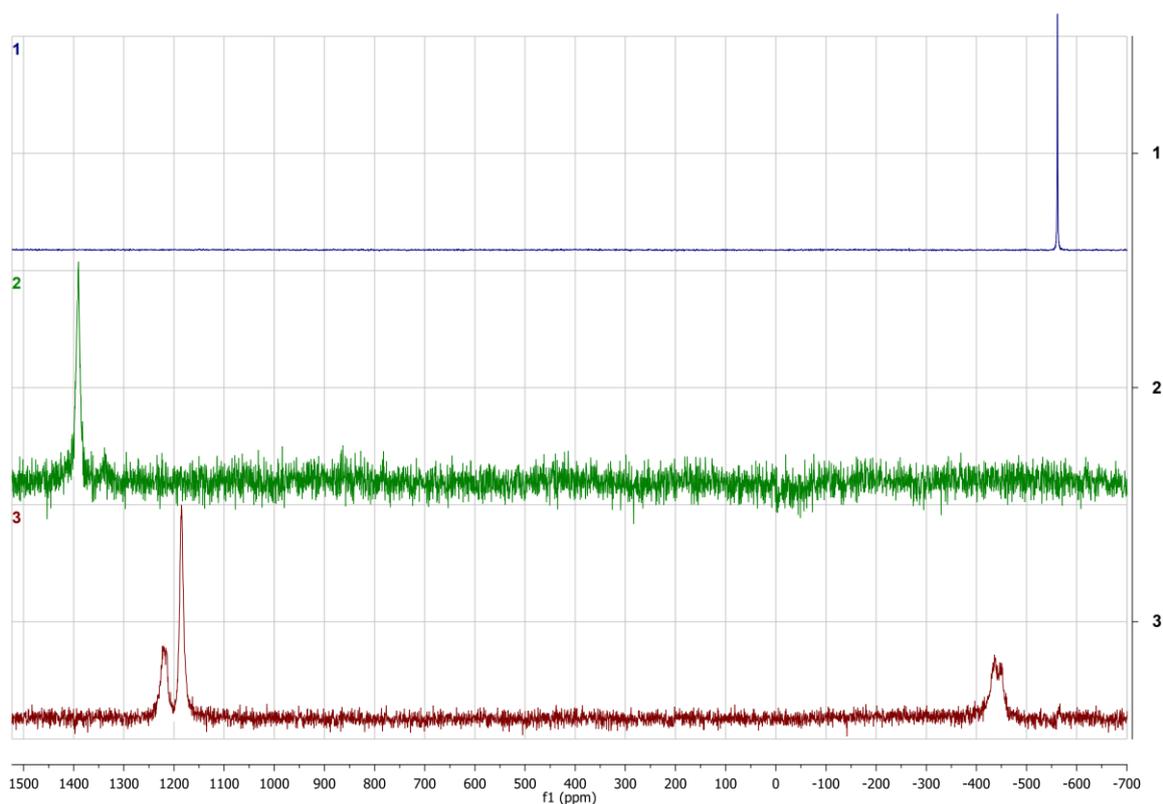
1 H₂O₂ may assist the dissociation, or leaching, of vanadium from vanadium-containing
 2 species, which then rapidly convert to catalytically active catecholato-bearing vanadium
 3 species *e.g.* [VO(3,5-DTBC)(3,5-DTBSQ)] and [V(3,5-DTBC)₃] in the presence of very large
 4 excess of catechol, 3,5-DTBQ and H₂O₂ relative to vanadium.[36,38] In a separate
 5 experiment, an iodometric assay was done to confirm the formation of hydrogen peroxide
 6 in our system.



7 **Figure 7.** Initial reaction rate of 4-TBC (0.1 M) oxidation over the period of 20 minutes in
 8 the presence of **3** (1×10^{-4} M) and/or several additives. See text for further information.
 9 Control 1: 0.1 M 4-TBC + 0.030 M H₂O₂ in the absence of **3**. Control 2: 0.1 M 4-TBC + **3**
 10 in the absence of H₂O₂. All measurements run in duplicate.

11 ⁵¹V NMR experiments were undertaken to determine qualitatively the nature of
 12 vanadium-containing species formed during catechol oxidation, and to gain some insight
 13 into the catalytically active vanadium species. In the experiments, 100 equivalents of 3,5-
 14 DTBC and 4-TBC were reacted with **3** in CDCl₃ at RT, and the ⁵¹V NMR spectra were
 15 recorded immediately. The ⁵¹V NMR spectra obtained from these experiments drastically
 16 differed from the original ⁵¹V NMR spectra of **3** (figure 8). In both cases, the original signal
 17 corresponding to **3** at *ca.* -562 ppm vanished completely, which is a clear indication of
 18 dynamic and very rapid changes to the first coordination sphere of **3**. New, very broad
 19 signals were observed at *ca.* +1221 and +1185 with 4-TBC and at *ca.* +1391 with 3,5-
 20 DTBC *viz.* significantly downfield relative to VOCl₃.

21



1 **Figure 8.** ^{51}V NMR spectra of 1) **3** in acetone- d_6 , 2) **3** + 100 eq. 3,5-DTBC in CDCl_3 . and 3)
2 **3** + 100 eq. 4-TBC in CDCl_3 .

3 These prominent changes, and the absence of ^{51}V NMR signals at approx. $-400 - (-600)$
4 ppm, the expected region for oxidovanadium(V) complexes bearing a redox-innocent NO_2
5 donor set, indicate that there are most likely no vanadium species bearing $\text{HL}^{\text{Saltris}}$
6 left.[33,68] In fact, the significantly downfield signals are almost certainly related to
7 diamagnetic catecholato-bearing vanadium species with at least two or even three
8 catechol ligands, since many reported non-innocent monocatecholato oxidovanadium(V)
9 systems with mixed ON donors appear upfield, and at best only slightly downfield of
10 VOCl_3 . [33] It should be noted, that the ^{51}V NMR spectra did not drastically change over a
11 period of two days. Furthermore, when 4-TBC was used a signal was observed at -438
12 ppm, only slightly downfield of **3**. This species has been tentatively assigned to
13 $[(\text{VO}(\text{HL}^{\text{Saltris}})(\text{O}-4\text{-TBC}))]$, where 4-TBC coordinates in a singly anionic monodentate
14 fashion. These assignments are in line with observations from ESI-MS studies (see
15 below), where bis- and tris(catecholato) oxidovanadium and non-oxidovanadium species
16 are detected.

17 To supplement the rather cautious assignments done in the ^{51}V NMR section above, the
18 same NMR samples were analyzed by ESI-HRMS in acetonitrile. Some reported
19 mechanistic studies investigating catechol oxidation by oxidovanadium complexes
20 frequently involve ESI-MS only in the positive mode.[20,23] However, as per the findings
21 by Finke and co-workers related to the nature of the true active catalyst, negative mode

1 MS studies might also reveal important information, and should always be run.[36]
2 Accordingly, we report both positive and negative MS results.

3 In the case of **3** + 3,5-DTBC, and in the negative mode, the main ionization product was
4 $[V(3,5\text{-DTBC})_3]^-$ at $m/z = 711.3884$ (calcd. $m/z = 711.3835$). Other species in the negative
5 mode are $[VO(3,5\text{-DTBC})_2]^-$ at $m/z = 507.2336$ (calcd. $m/z = 507.2321$). A very low-
6 intensity signal can be observed for $[VO(\text{HL}^{\text{Saltris}})(3,5\text{-DTBC})]^-$ at $m/z = 622.2976$ (calcd.
7 $m/z = 622.2954$). In the positive mode the only clearly detected species is $[3,5\text{-DTBQ} +$
8 $\text{Na}]^+$ at $m/z = 243.1400$ (calcd. $m/z = 243.1356$). However, there exists a very low-
9 intensity (*ca.* 2 %) signal at $m/z = 646.2889$. We have tentatively assigned this to the
10 species $[VO(\text{H}_2\text{L}^{\text{Saltris}})(O\text{-}3,5\text{-DTBC}) + \text{Na}]^+$, which has a calculated $m/z = 646.2919$. There
11 are no traces of the intact **3** in either positive or negative polarization. From this data, the
12 detection of $[VO(3,5\text{-DTBC})_2]^-$ or, perhaps $[V(\text{IV})O(3,5\text{-DTBC})(3,5\text{-DTBSQ})]^-$, is
13 significant, as it has been linked to the Pierpont's complex $[V(\text{V})O(3,5\text{-DTBC})(3,5\text{-}$
14 $\text{DTBSQ})]_2$, which is the dimerized resting state of the supposed active catalyst $[VO(3,5\text{-}$
15 $\text{DTBC})(3,5\text{-DTBSQ})]$. [38] Pierpont's complex, having a calculated $m/z = 1014.4631$, is not
16 detected, however. The MS spectra are presented in the ESI (figures S42–43).

17 With **3** + 4-TBC, a somewhat similar speciation is observed, however, the main species in
18 the negative ionization corresponds to $[VO(\text{HL}^{\text{Saltris}})(O\text{-}4\text{-TBC})]^-$ at $m/z = 566.2312$
19 (calcd. $m/z = 566.2328$). The tris catecholato species $[V(4\text{-TBC})_3]^-$ is also present at m/z
20 $= 543.1966$ (calcd. $m/z = 543.1957$) with low intensity. These findings may suggest that
21 in the presence of 4-TBC, which reacts slower than 3,5-DTBC, **3** is somewhat more
22 inclined to form monocatecholato adducts. This would also give some credibility to the
23 ^{51}V NMR assignment at -438 ppm (see above). Similarly to the above case, the
24 $[VO(\text{H}_2\text{L}^{\text{Saltris}})(O\text{-}4\text{-TBC}) + \text{Na}]^+$ low-intensity adduct is tentatively assigned to the $m/z =$
25 590.2240 observed in the positive mode (calcd. $m/z = 590.2293$). $[\text{3} + \text{Na}]^+$ is also
26 detected in the positive ionization mode with $m/z = 825.2625$ (calcd. $m/z = 825.2706$)
27 unlike previously in the presence of 3,5-DTBC. The MS spectra are presented in the ESI
28 (figures S44–S45).

29 After overnight reaction of 3,5-DTBC in the presence of 1 mol-% **3** three compounds were
30 isolated (table 5 and ESI). The product distribution resembles that found in many 3,5-
31 DTBC oxidation reactions catalyzed by a variety of different vanadium pre-
32 catalysts.[35,36,38] For instance, the 7-membered 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-
33 diene-2,7-dione (**4**) is generally obtained with the highest yield of 40–57 % of the
34 reaction products. While our isolated yield falls slightly short of 40 %, it is still the main
35 product at 31 % yield. The second to most abundant product is 3,5-di-*tert*-butyl-1,2-
36 benzoquinone (**5**) with a mean yield of 9–25 % and agrees with our observations (yield
37 = 23 %). Additionally, the dimeric 4',6,6',8-tetra-*tert*-butyl-3*H*-spiro[benzo[*b*][1,4]di-
38 oxine-2,2'-pyran]-3-one (**6**) represents one of the low-yielding products (10–18 %), a fact
39 which is also observed by us (18 % yield). However, we were unable to isolate, nor detect,
40 the lactones 3,5-di-*tert*-butyl-2-pyrone (**7**) or 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-
41 furanone (**8**) which generally, and in combination, represent at most 20 % of the total

1 product yield. Accordingly, they might represent the “missing” 28 %, as the combined
 2 *isolated* yield of our reaction amounts to only 72 %. TLC was however used to establish
 3 that no 3,5-DTBC was present, and hence we estimate a minimum 95 % conversion. It is
 4 important to emphasize that the formation of the products **4**, **6**, **7** and **8**, which represent
 5 the dioxygenase intra- and extradiol cleavage products, have been linked[36,38] to the
 6 vanadium species $[V(3,5\text{-DTBC})_3]^-$ (detected with ESI-HRMS, see above), which is itself
 7 intimately related to $[VO(3,5\text{-DTBC})(3,5\text{-DTBSQ})]$ and the “common catalyst
 8 hypothesis”.[36]

Table 5. The product distribution obtained by reacting 3,5-DTBC with air in boiling chloroform in the presence of 1 mol-% **3**.

Estimated conversion ^a (%)	Isolated product yield (%)				
	4	5	6	7	8
≥95	31	23	18	nd ^b	nd ^b

^a As determined by TLC. ^b Not detected. Reaction conditions: 500 mg 3,5-DTBC, 18 mg **3**, 30 mL CHCl₃, reflux 16 h.

9 The mechanistic investigations described above provide compelling evidence in support
 10 of the notion that neither **3**, nor a close structural derivative thereof, is the active catechol
 11 oxidation catalyst. Consequently, a catalytic cycle resembling the one described for the
 12 closely similar dicobalt system cannot be credibly proposed.[28] Instead, the results
 13 obtained from UV-Vis, ⁵¹V NMR, and from the ESI-HRMS and product distribution
 14 experiments in particular, confer a rather different state of affairs. The combined results
 15 clearly indicate that dioxygenase activity is presented during catalysis as well, and that
 16 the system presented herein confers very similar behavior to many other vanadium
 17 precatalysts. These results are decisively in favor of the “common catalyst
 18 hypothesis”.[36]

19 Oxygen atom transfer activity

20 *cis*-Dioxidomolybdenum(VI) and -tungsten(VI) complexes are well known to catalyze
 21 oxygen atom transfer (OAT) to suitable organic substrates such as, but not limited to,
 22 benzoin and triphenylphosphine.[82–86] The propensity of Mo/W compounds to
 23 catalyze this particular reaction is not at all surprising considering the role of these
 24 metals in enzymes such as DMSO reductase that catalyzes similar reactions.[86] As a

1 result, oxidovanadium complexes have generally received much less attention in this
2 regard. We chose tris(4-fluorophenyl)phosphine as the model compound, due to the ease
3 of monitoring of the reaction by the very sensitive and quantitative ^{19}F NMR.[55] Quite
4 unexpectedly, however, the complexes were found to not have any significant OAT
5 activity, even at moderate catalyst loadings of 10 mol-% (ESI figure S58).

6 **Conclusions**

7 Mononuclear complexes $[\text{MO}_2(\text{H}_2\text{L}^{\text{Saltris}})]$ ($\text{M} = \text{Mo}$ (**1**), W (**2**)), as well as a dinuclear
8 complex $[\text{VO}(\text{HL}^{\text{Saltris}})]_2$ (**3**) with a hydroxyl-rich Schiff base proligand *N*-(1,3-dihydroxy-
9 2-(hydroxymethyl)propan-2-yl)-3,5-di-*tert*-butylsalicylaldehyde ($\text{H}_4\text{L}^{\text{Saltris}}$), were pre-
10 pared by the reaction with Mo, W and V metal precursors in methanol solutions. The
11 dinuclear vanadium complex shows moderate activity in the oxidation of 4-TBC and 3,5-
12 DTBC, mimicking the action of the dicopper enzyme catechol oxidase. Strikingly, the
13 activity of **3** in catechol oxidation was observed to be similar to that of a structurally very
14 similar dicobalt complex $[\text{Co}(\text{H}_2\text{L}^{\text{Saltris}})(\text{OAc})]_2$, whose mechanism of catalysis has been
15 established. However, a set of experiments investigating the catechol oxidation
16 mechanism by **3**, prompted by similarity to $[\text{Co}(\text{H}_2\text{L}^{\text{Saltris}})(\text{OAc})]_2$, strongly hint that **3** is
17 not the catalytically active species in the solution. Rather, the presented mechanistic
18 studies reinforce a strong argument in the literature which suggests that a catecholato-
19 bearing vanadium species is formed *in-situ* during catalytic turnover conditions in the
20 presence of 3,5-DTBC, is in fact the real active catalyst. It is further proposed, that such a
21 complex is formed in virtually every scenario involving vanadium-based precatalysts and
22 3,5-DTBC, a fact clearly demonstrated by the $[\text{VO}(\text{HL}^{\text{Saltris}})]_2$ system presented herein.
23 Furthermore, and quite unexpectedly, the complexes were revealed not to demonstrate
24 any significant OAT activity in the oxidation of $(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)_3$, even when moderate
25 catalyst loadings were employed.

26 **Conflicts of interest**

27 The authors declare no competing interests.

28 **Electronic Supplementary Information**

29 All spectra relevant to the characterization of the compounds are presented in the ESI,
30 as well as detailed descriptions of the syntheses.

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