Synthesis of new oxido-vanadium complexes: catalytic properties and cytotoxicity

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Reaction of 2,3-dihydroxy benzaldehyde with 2-({2-amino phenyl}diazenyl)phenol afforded the ligand 3-(2-(2-hydroxyphenyl)diazenyl)-4-alkylphenyliminomethyl)benzene-1,2-diol. Reaction of H_2L with $VOSO_4$. $5H_2O$ gave the oxido-vanadium(IV) complexes [(L)VO], which exhibited a quasi-reversible oxidative cyclic voltammetric response in a V(IV)/V(V) oxidative process. The complexes act as catalysts in the oxidation of organic thioethers and bromination of phenol. Their cytotoxic properties were examined for three cancer cell lines.

Keywords: oxido-vanadium, sulfide oxidation, phenol bromination, cytotoxic properties

Oxido-vanadium(IV) complexes have been recognised to occur in the active sites of several vanadium-containing enzymes.[1–6] Vanadium haloperoxidase is one of the important vanadium-containing proteins.[7–14] Amavadine contains oxido-vanadium(IV) complexes having good electron transfer properties and stability against hydrolysis.[15–17] In mushrooms, amavadine acts as an electron transfer centre mediating thiol oxidation in the absence of peroxide. A number of vanadium(IV) and vanadium(V) complexes with N,O donor ligands have been examined for potential medicinal applications.[18–32] The anticancer activity of a few oxido-vanadium(IV) complexes encouraged us to prepare new oxido-vanadium(IV) complexes incorporating N,O donor ligands with reversible electron transfer properties. This work stems from our interest in the vanadium chemistry of azosalen ligands. It is worthwhile mentioning that the oxido-vanadium(IV) complexes of such ligands exhibit interesting electron transfer, catalytic and cytotoxic properties. Therefore, we report here several new analogues of azosalen ligands as well as the chemistry of the derived oxido-vanadium(IV) complexes. The new ligands were designed in such a way that the free uncoordinated phenolic group in the ligand backbone could act either to form polynuclear V(IV) complexes or to enhance the possibility of hydrogen bond formation with polar biomolecules for suitable interactions.

The activity of the new complexes in the oxidation of organic thioethers and bromination of phenol was studied, and their cytotoxic properties against a breast cancer cell (MCF7) line were also examined.

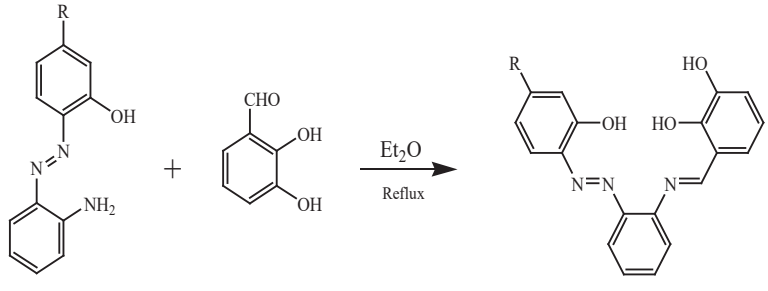
Results and discussion

The ligands **1a**, **1b** and **1c** were prepared by refluxing 2,3-dihydroxybenzaldehyde with 2-({2-aminophenyl}diazenyl) phenol in diethyl ether (Scheme 1).

Slow evaporation of solvent afforded the crystalline (E)-2-({2-aminophenyl}diazenyl)-5-alkylphenols, which were collected and used without further purification. In this paper, for ease of representation, **1a**, **1b** and **1c** have been abbreviated as H_2L^1, H_2L^2 and H_2L^3, respectively, where H represents the ionisable phenolic protons upon complexation. Reaction of $VOSO_4$ with H_2L in refluxing methanol afforded brown-coloured crystalline complexes **2a, 2b** and **2c**, which for clarity will be abbreviated as [(L^1)VO], [(L^2)VO] and [(L^3)VO], respectively (Scheme 2).

The UV-Vis spectra of the H_2L ligands exhibited a broad absorption within the range 300–500 nm, with absorbance maxima near 315 nm and a shoulder near 400 nm.[33] The corresponding [(L)VO] complexes exhibited three absorption maxima, near 345, 375 and 485 nm.

The IR spectra of the H_2L ligands displayed two distinct absorptions near 1618 and 1466 cm^{-1} for ν_{CN} of azomethine (–CH=N–) and $\nu_{N=N}$ of diazo (–N=N–), respectively, which shifted to lower frequencies (1611 cm^{-1} and 1432 cm^{-1}, respectively) upon complexation.[34–38] Although there are three phenolic OH groups in the ligands, only one absorption near 3470 cm^{-1} could be observed. In the case of the (L)VO complexes, ν_{OH} of the free phenolic group was near 3450 cm^{-1}. The ν_{VO} was near 978 cm^{-1} for all of the [($L^{1–3}$)VO] complexes.[33]



HL

Compound	R	Abbreviation
1a	H	H_2L^1
1b	CH_3	H_2L^2
1c	Cl	H_2L^3

Scheme 1 Synthesis of H_2L ligands.

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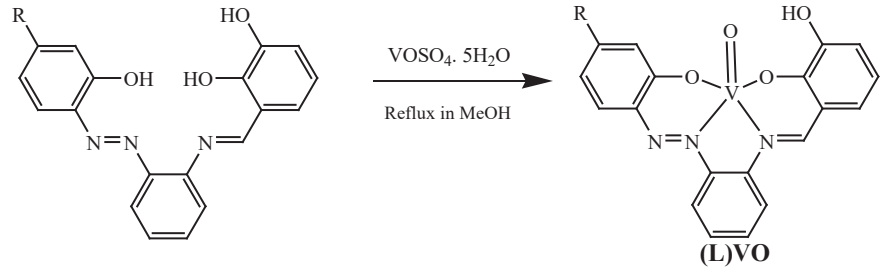


Compound	R	Abbreviation
2a	H	$(L^1)VO$
2b	CH_3	$(L^2)VO$
2c	Cl	$(L^3)VO$

Scheme 2 Preparation of vanadium complexes.

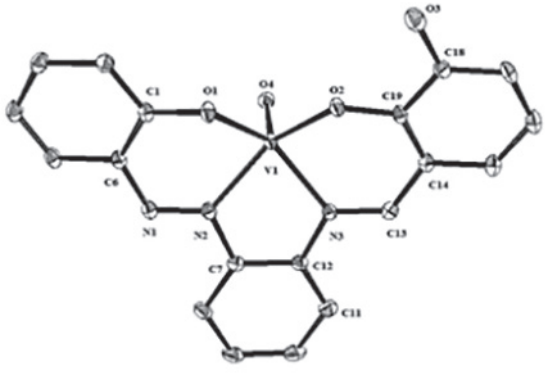


Fig. 1 Ortep plot of [(L^1)VO] with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths and angles for compound **2a**

Bond lengths (Å)			
V(1)–O(1)	1.9211(13)	O(1)–C(1)	1.324(2)
V(1)–O(2)	1.9277(13)	N(1)–N(2)	1.281(2)
V(1)–O(4)	1.5990(14)	N(1)–C(6)	1.385(2)
V(1)–N(2)	2.0628(16)	N(2)–C(7)	1.423(2)
V(1)–N(3)	2.0514(16)	N(3)–C(12)	1.424(2)
O(2)–C(19)	1.330(2)	N(3)–C(13)	1.307(2)
Bond angles (°)			
O1–V1–O2	88.11(6)	O1–V1–N2	85.45(6)
O1–V1–O4	109.14(6)	O2–V1–O4	109.33(6)
O1–V1–N3	144.53(6)	O2–V1–N2	148.10(6)
O2–V1–N3	88.71(6)	O4–V1–N2	102.28(7)
O4–V1–N3	105.22(7)	N2–V1–N3	78.89(6)
V1–O2–C19	127.11(12)	V1–O1–C1	122.63(11)
N2–C7–C12	114.76(16)		

The ^{1}H NMR spectra of the ligands displayed three resonances in the range of δ values 12.87–13.09, 11.54–11.64 and 9.21–9.38 for the three free phenolic protons.[38] The azomethine proton (–CH=N–) signal appeared within the range 8.90–9.05.[38] The spectra for other aromatic protons appeared within the range 6.74–7.99, and the number of protons and their patterns were consistent with the proposed composition. UV-Vis, IR and ^{1}H NMR data are collected together in the experimental section. Figures showing the ^{1}H NMR spectra are given in the electronic supplementary material (ESI).

The crystal structure of [(L^1)VO] was determined as representative for unequivocal characterisation. The molecular structure contains the V(IV) metal ion in a distorted square pyramidal ligand field, where the square plane is constituted by the NNOO donors of the $(L^1)^{2-}$ ligand and the axial position is occupied by the oxido-ligand.

The V–O bond length (1.5999 Å) is shorter than the V–O single bond (1.9277 Å), indicating a higher VO bond order as expected.[33]

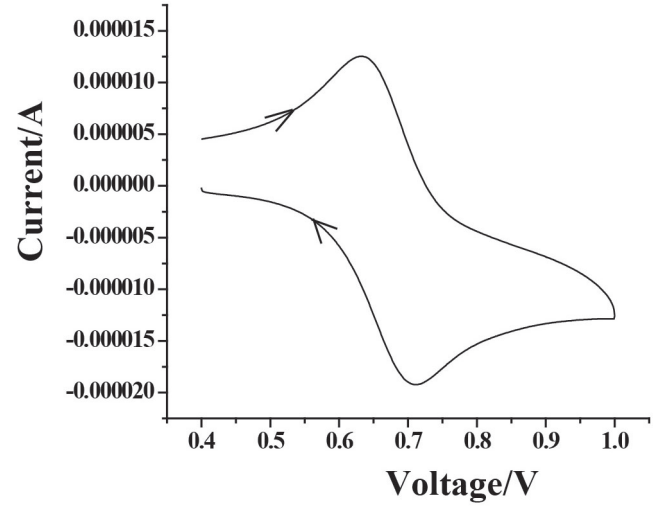


Fig. 2 Cyclic voltammogram of [(L^1)VO] in CH_3CN–CH_2Cl_2 mixed solvent.

Table 2 Oxidation of sulfides catalysed by [(L^1)VO] in methanol–dichloromethane (9:1)

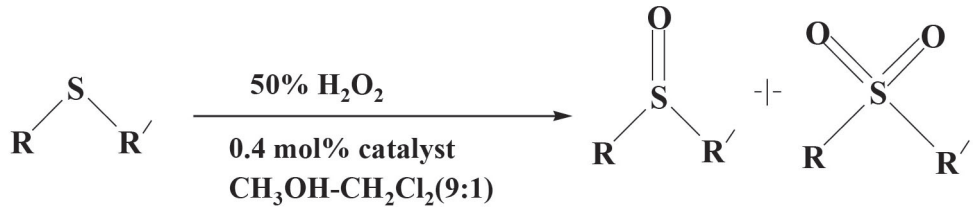
Entry	H_2O_2 (equiv.)	Time (h)	Yield (%)	
			Sulfoxide	Sulfone
Ph–S–CH_3	5	2.5	45	55
Ph–S–CH_2Ph	5	2.5	60	30
Ph–S–CH_2–CH=CH_2	5	2.5	35	45
Ph–S–Ph	5	2.5	40	50

The vanadium ion is displaced towards the oxido-ligand with a deviation of 0.454 Å from the square plane (0.0241 Å) formed by the four NNOO donors of the $(L^1)^{2-}$ ligand. The bond lengths and angles are presented in Table 1.

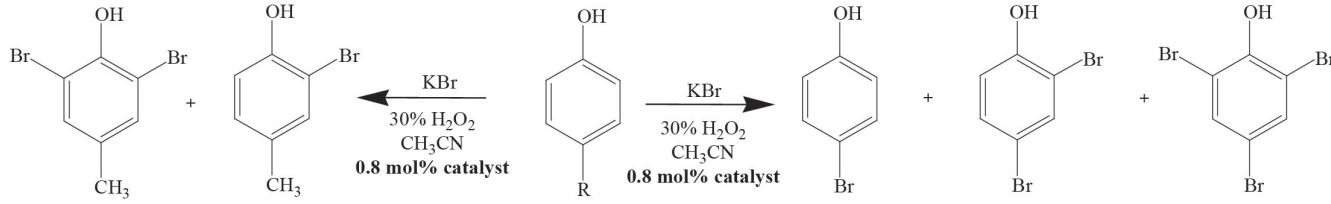
The [(L^1)VO] complex exhibited a quasi-reversible oxidative cyclic voltammetric response at $E_{1/2}$ = 0.67 V *vs* SCE, which was assigned to a V(IV)/V(V) oxidative process.[33] It is worthwhile mentioning that there was no reversible reductive response, unlike the similar complex reported earlier.[33]

All of the complexes displayed magnetic moments of one equivalent electron, which is consistent with the V(IV) oxidation state.

A few organic sulfides have been oxidised by H_2O_2 using [(L^1)VO] as catalyst, and the results are given in Table 2. Formation of mono-oxygenated sulfoxides and dioxygenated sufones occurred, but selective oxidation to form only sulfoxides did not take place.



Scheme 3 Oxidation of sulfides catalysed by [(L^1)VO].



R=H for phenol
R=CH_3 for *p*-cresol

Scheme 4 Bromination of phenolic compounds using [(L^1)VO] as catalyst.

Table 3 Bromination of phenolic compounds by bromide and peroxide using [(L^1)VO] as catalyst

Entry	H_2O_2 (equiv.)	Time (h)	Yield (%)		
			Mono-bromo	Di-bromo	Tri-bromo
Phenol	5	20	13	27	41
p-Cresol	5	20	30	40	–

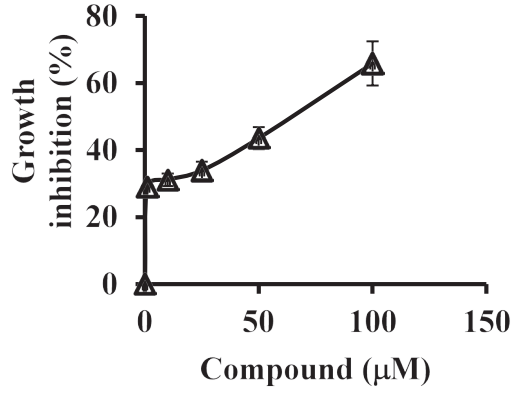


Fig. 3 Effect of [(L^1)VO] on growth of breast cancer cell line MCF7.

Products were isolated to calculate the yields and for characterisation. The characterisations of the sulfoxides and sulfones were carried out by matching the IR spectra.

Bromination of aromatic moieties *in vivo* by bromide and peroxide in the presence of the vanadium-containing bromoperoxidase enzyme is well documented in the literature.[7,39–42] Thus, brominations of phenolic compounds *in vitro* by bromide and peroxide in the presence of vanadium complexes have been examined in the search for a potential catalyst for such bromination. In this context, the complex [(L^1)VO] has been used as catalyst for bromination of phenol and *p*-cresol. Both phenolic compounds were brominated up to 70% and 80% extent. The yields were calculated after isolating the products (Scheme 4 and Table 3).

IC_{50} determination

The complex [(L^1)VO] was found to be effective in suppressing the growth of human breast cancer cells (MCF7 and MDA-MB-231 cell lines) and human colon cancer cells (HCT116) (Figs. 2, 3 and 4, respectively). The IC_{50} values were found to be 64.67 ± 9.01, 49.33 ± 6 and 39.03 ± 1.1 for the MCF7, MDA-MB-231 and HCT116 cell lines, respectively.

Table 4 IC50 determination of [(L^1)VO]

Sr no.	Cell line	Compound	IC50 (μM)
1	MCF7	[(L^1)VO]	64.67 ± 9.01
2	MDA-MB-231	[(L^1)VO]	49.33 ± 6.1
3	HCT-116	[(L^1)VO]	39.03 ± 1.1

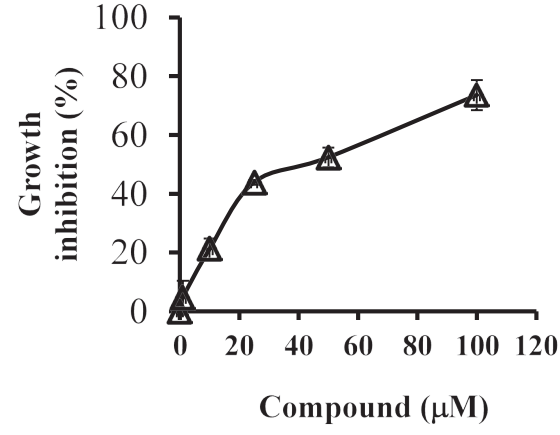


Fig. 4 Effect of [(L^1)VO] on growth of breast cancer cell line MDA-MB-231.

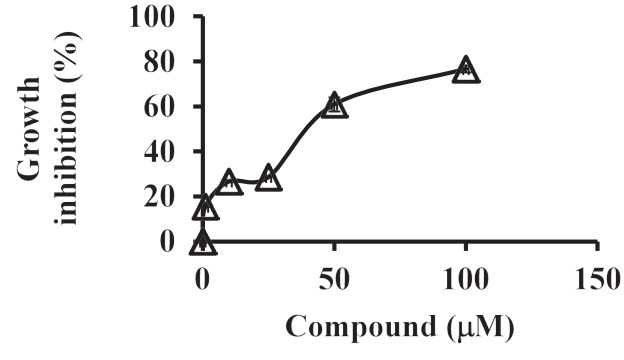


Fig. 5 Effect of [(L^1)VO] on growth of breast cancer cell line HCT116.

Experimental

The solvents used in the reactions were of reagent grade (E. Merck, Kolkata, India) and were purified and dried using previously reported procedures.[43] $VOSO_4.5H_2O$ was purchased from E. Merck (Kolkata, India) and was used as received. The ligands 2-({2-aminoaryl} diazenyl) phenol were prepared following previously reported procedures.[38] Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 C, H, N, S/O series II elemental analyser. IR spectra were recorded as KBr pellets on a Perkin-Elmer L120-00A FT-IR spectrometer. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker 400 NMR spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Electrochemical measurements were made under dinitrogen using a CH instruments model 600D potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. 2,3-Dihydroxybenzaldehyde, the human breast cancer cells (MCF7 and MDA-MB-231), DMEM medium and HCT116 colon cancer cells, RPMI-1650 medium, penicillin (100 μg mL^{-1}) and streptomycin sulfate (100 μg mL^{-1}) were all purchased from Sigma-Aldrich (USA), as was 10% foetal bovine serum (FBS).

All of the ligands **1a**, **1b** and **1c** were prepared following similar procedures. A representative procedure for **1a** is given below.

Synthesis of H_2L^1 (**1a**): A mixture of 2-({2-aminophenyl}diazenyl) phenol (2.13 g, 10 mmol) and 2,3-dihydroxybenzaldehyde (1.38g, 10 mmol) in dry diethyl ether (100 mL) was refluxed for 12 h. Reddish-brown crystalline solid **1a** was obtained on slow evaporation of the solvent.

3-(2-(2-Hydroxyphenyl)diazenyl)phenyliminomethyl)benzene-1,2-diol (**1a**): Isolated yield: 3.3 g (94%); Anal. calcd for $C_{19}H_{15}N_3O_3$ (333): C, 68.46; H, 4.54; N, 12.61; found: C, 68.48; H, 4.51; N, 12.68%; UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 402^{sh} (5894), 312 (13420); IR (KBr) (ν_{max}/cm^{-1}): 1466 (N=N), 1618.75 (CH=N), 3468.43 (OH); ^{1}H NMR (DMSO-d_6): δ 13.09 (s, OH), 11.54 (s, OH), 9.38(s, OH), 9.05(s, CH=N), 7.99 (d, 1H), 7.87 (d, 1H), 7.72(t, 1H), 7.66 (d, 1H), 7.54–7.47 (m, 2H), 7.23 (d, 1H), 7.13 (d, 1H), 7.11 (t, 1H), 7.04 (d, 1H), 6.87 (t, 1H).

3-(2-(2-Hydroxyphenyl)diazenyl)-4-methyl-phenyliminomethyl) benzene-1,2-diol H_2L^2 (**1b**) *and 3-(2-(2-hydroxyphenyl)diazenyl)-4-chloro-phenyliminomethyl)benzene-1,2-diol H_2L^3* (**1c**): **1b** and **1c** were prepared following the same procedure as described for **1a**, using 2-({2-aminophenyl}diazenyl)-5-methylphenol and 2-({2-aminophenyl} diazenyl)-5-chlorophenol in place of 2-({2-aminophenyl}diazenyl)phenol, respectively.

(**1b**): Isolated yield: 3.32 g (91%); Anal. calcd for $C_{20}H_{17}N_3O_3$ (347.4): C, 69.14; H, 4.94; N, 12.1; found: C, 69.02; H, 4.88; N, 12.18%; UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 321 (15020), 400^{sh} (7876); IR (KBr) (ν_{max}/cm^{-1}): 1466.99 (N=N), 1618.47 (C=N), 3475.40 (O–H); ^{1}H NMR (DMSO-d_6): δ 12.87 (s, OH), 11.64 (s, OH), 9.26(s, OH), 8.90 (s, CH=N), 7.84 (d, 1H), 7.66 (d, 1H), 7.55 (t, 1H), 7.51 (d, 1H), 7.38 (t, 1H), 7.10 (d, 1H), 6.91 (d, 1H), 6.81 (s, 2H), 6.79 (d, 1H), 6.74 (t, 1H), 2.43 (t, 3H).

(**1c**): Isolated yield: 3.28 g (85%); Anal. calcd for $C_{19}H_{14}N_3O_3Cl$ (367.8): C, 62.04; H, 3.84; N, 11.43; found: C, 61.96; H, 3.79; N, 11.55%; UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 319 (10014), 392^{sh} (5911); IR (KBr) (ν_{max}/cm^{-1}): 1467.80 (N=N), 1618.82 (C=N), 3474.99 (O–H); ^{1}H NMR (DMSO-d_6): δ 13.20 (s, OH), 11.57 (s, OH), 9.21 (s, OH), 8.93 (s, CH=N), 7.86 (d, 2H), 7.71 (d, 1H), 7.58 (t, 1H), 7.56 (d, 1H), 7.40 (t, 1H), 7.10 (s, 1H), 7.08 (d, 1H), 7.00 (d, 1H), 6.91 (d, 1H), 6.72 (t, 1H).

Synthesis of [(L)VO]: The complexes [(L^1)VO] (**2a**), [(L^2)VO] (**2b**) and [(L^3)VO] (**2c**) were prepared following similar procedures. A representative procedure for **2a** is given below.

[(2-Hydroxy-6-(2-(2-oxido-4-alkyl-phenyl)diazenylphenylimino) methylphenolate)oxidovanadium(IV)-N,N,O,O] [(L^1)VO] (**2a**): A drop of water was added to dissolve $VOSO_4.5H_2O$ (0.125 g, 0.5 mmol) and then methanol (5 mL) was added. The solution of $VOSO_4$ was then added to a solution of H_2L^1 (0.165 g, 0.5 mmol) in methanol (20 mL) and the mixture was refluxed for 15 min. The dark brown-coloured solid product was separated by filtration and the solid mass was dissolved in dichloromethane. Single crystals were obtained by slow evaporation of the solvent. Isolated yield: 0.19 g (65%); Anal. calcd for $C_{19}H_{13}N_3O_4V$ (398.27): C, 57.30; H, 3.29; N, 10.55; found: C, 57.34; H, 3.18; N, 10.68%; UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 486 (8413), 375^{sh} (16329), 343 (20760), 240 (23299); IR (KBr) (ν_{max}/cm^{-1}): 1438 (N=N), 1618 (C=N), 3450 (O–H), 978 (V=O).

[(L^2)VO] (**2b**) *and [(L^3)VO]* (**2c**): Complexes [(L^2)VO] (**2b**) and [(L^3)VO] (**2c**) were prepared using H_2L^2 and H_2L^3 in place of H_2L^1, respectively.

[(2-Hydroxy-6-(2-(2-oxido-4-methyl-phenyl)diazenylphenylimino) methylphenolate)oxidovanadium(IV)-N,N,O,O] [(L^2)VO] (**2b**): Isolated yield: 0.18 g (61%); Anal. calcd for $C_{20}H_{15}N_3O_4V$ (412.32): C, 58.26; H, 3.67; N, 10.19; found: C, 58.12; H, 3.63; N, 10.23%; UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 489 (12664), 378^{sh} (21382), 348 (25093), 243 (26094); IR (KBr) (ν_{max}/cm^{-1}): 1432 (N=N), 1611 (C=N), 3446 (O–H), 978 (V=O).

[(2-Hydroxy-6-(2-(2-oxido-4-chloro-phenyl)diazenylphenylimino) methylphenolate)oxidovanadium(IV)-N,N,O,O] [(L^3)VO] (**2c**): Isolated yield: 0.19 mg (62%); Anal. calcd for $C_{19}H_{12}N_3O_4ClV$ (432.73): C, 52.73; H, 2.80; N, 9.71; found: C, 52.71; H, 2.77; N, 9.75%: UV-Vis spectrum (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) 481 (31849), 370^{sh} (52966), 347 (60755), 264 (45783), 239 (64563); IR (KBr) (ν_{max}/cm^{-1}): 1430 (N=N), 1615 (C=N), 3443 (O–H), 977 (V=O).

Catalytic oxygenation of thioethers

To a solution of PhSMe (465 mg, 3.75 mmol) in methanol–dichloromethane (10:90 v/v), the catalyst [(L^1)VO] (6.0 mg, 0.015 mmol) and 50% H_2O_2 (1 mL) were added at 0 °C. The mixture was stirred for 2.5 h keeping the temperature at 0–4 °C. The solution was then dried in a vacuum. The products were isolated by thin layer chromatography (TLC). The solid PhSOMe and $PhSO_2Me$ were isolated as the third and second fractions, respectively, with yields of 187 mg and 222 mg, respectively. The products were characterised by IR spectroscopy. The results of the conversions of other thioethers to sulfoxides and sulfones are given in Table 2.

Bromination of aromatic alcohols

Complex **2a** (6 mg, 0.015 mmol) and *p*-cresol (198 mg, 1.8 mmol) were dissolved in CH_3CN (10 mL). To this mixture, KBr (440mg, 3.7 mmol) dissolved in water (2 mL) was added, followed by 30% H_2O_2 (1 mL) added dropwise with constant stirring. The pH of the solution was adjusted to approximately 3 by dropwise addition of 2N HCl solution. The reaction mixture was stirred for 20 h at room temperature. The product was extracted with diethyl ether and concentrated to about 1 mL. Two products, 2-bromo-4-methylphenol and 2,6-dibromo-4-methylphenol, were separated by TLC and characterised by spectroscopic techniques. The isolated yields were 79 mg and 60 mg, respectively. The results of the conversions are given in Table 3. The same reaction was carried out keeping all other components and conditions the same but not adding the catalyst.

Biological activity

Cell lines: Human breast cancer cells (MCF7 and MDA-MB-231) were grown in DMEM medium, and HCT116 colon cancer cell cells were grown as a monolayer in RPMI-1650 medium fortified with antibiotics (penicillin 100 μg mL^{-1}, streptomycin sulfate (100 μg mL^{-1}) and 10% foetal bovine serum (FBS) at 37 °C, 5% CO_2 atmosphere in humid conditions (Table 4).

Determination of 50% inhibitory concentration (IC_{50})

The cytotoxic effect of [(L^1)VO] on MCF7, MDA-MB-231 and HCT116 was evaluated by MTT (3-{4,5-dimethylthiazol-2-yl}-2,5-diphenyltetrazolium bromide) assay.[44–47] Cells of the required cell line were seeded in a 96-well plate (5×10^3 cells/well) and allowed to adhere for the next 24 h. The cells were then treated with different

Table 5 Crystallographic data for [(L^1)VO]

Empirical formula	$C_{19}H_{13}N_3O_4V$
Formula weight	398.26
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a/Å	10.2000(4)
b/Å	9.3314(4)
c/Å	17.7691(7)
α/deg.	90
β/deg.	106.145(2)
γ/deg.	90
Volume/Å^3	1624.57(12)
F(000)	812
Z	4
Temperature/K	293
Mu (MoKα) (mm)	0.644
R_1 (all data)	0.0359
wR_2 [$I > 2\sigma(I)$]	0.1008
Goodness-of-fit on F^2	1.11

concentrations (0–100 μM) of the complexes for 48 h. After completion of incubation with the compounds, MTT solution (20 μL/well from stock of 5 mg mL^{-1}) was added to each well and incubated for 4 h in a humid 5% CO_2 incubator. Media-containing MTT solutions were then replaced with 100 μL/well MTT solvent [isopropanol, HCl (4 mM) and triton X-100 (0.01%)] and incubated in the dark for 10–15 min with gentle rocking at room temperature. The absorbance of the solution in each well was then measured in an Elisa plate reader (Thermo scientific MULTISKAN GO V3.2) at 590 nm. All experiments were carried out as four biological replicates. DMSO-treated cells were used as the control in each experiment. The percentage viability of treated cells over the control was evaluated for assessing the cytotoxicity of the compounds on cancerous cells.

Crystallography

A single crystal of **2a** was grown by slow evaporation of a methanol solution at 298 K. Data were collected by the ω-scan technique on a Bruker Smart CCD diffractometer with Mo-Kα radiation monochromated by a graphite crystal. Structure solution was accomplished by direct methods using the SHELXS-97 program.[48,49] Full matrix least squares refinements on F^2 were performed using the same program.[48,49] All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions. The data collection parameters and relevant crystal data are presented in Table 5.

Supplementary data

CCDC 1572035 contains the supplementary crystallographic data for compound **2a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic supplementary information (ESI)

Figs S1–S6 show the UV-Vis spectra of the ligands and complexes, Figs S7–S12 show the IR spectra of the ligands and complexes, and Figs S13–S15 show the ^{1}H NMR spectra of the ligands. The ESI is available through http://ingentaconnect.com/content/stl/jcr/2018/00000042/00000001/art00014

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