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Oxidovanadium complexes with tetradentate Schiff bases: Synthesis, structural, electrochemical and catalytic studies

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ABSTRACT

A series of new tridentate Schiff base ligands derived from the condensation of 4,5-dinitro-1,2-phenylenediamine and various salicylaldehyde derivatives was synthesized and characterized by common spectroscopic and analytical methods. Oxidovanadium(IV) complexes of tetradentate Schiff base ligands derived from the condensation of this diamine and salicylaldehyde derivatives were also synthesized by template method and were characterized. The crystal structures of a tridentate ligand, HL², and one of the complexes, VOLig², were determined by X-ray crystallography. HL² crystallizes in triclinic space group $P\bar{1}$, while the VOLig² (which crystallizes as the DMF solvate) in monoclinic space group $P2_1/n$ with two [VOLig²] DMF symmetry-independent units per asymmetric part of the unit cell. The electrochemical properties of these complexes were studied by cyclic voltammetry which shows quasi-reversible V^{IV}/V^V redox process. The new complexes are also used as catalysts for the selective oxidation of cyclooctene with tert-butylhydroperoxide (TBHP) and H₂O₂ in acetonitrile. High catalytic activities were observed and excellent selectivity was found for the epoxidation of cyclooctene.

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1. Introduction

One of the major goals in recent chemistry is to find new and efficient catalysts for the industrially important reactions [1-6]. Considering this, oxidovanadium(IV) Schiff base complexes have received extensive attention due to their catalytic properties [7–10]. These complexes are considered as multipurpose molecules because of their interesting spectroscopic [11], biological [12-13], mechanochemical [14] and many other activities and characteristics [15-19]. One of the most widely studied characteristics of these complexes is their ability to catalyze the epoxidation reaction of olefins. The epoxidation products are among the most widely used and important intermediates in the laboratory syntheses and chemical industries. We and other collaborators have previously shown that the catalytic efficiency of oxidovanadium(IV) tetradentate Schiff base complexes in this epoxidation reaction increases with the increase in the E⁰ of V^{IV}/V^{V} couple [20–21]. We have previously shown that the presence of electronegative groups in the ancillary ligands increases this E⁰ and therefore increases the catalytic efficiency of these complexes [21]. Herein, we report the synthesis and characterization of a series of new tridentate Schiff base ligands from the condensation of 4,5-dinitro-1,2-phenylenediamine and various salicylaldehyde derivatives, as well as oxidovanadium(IV) complexes of a series of tetradentate Schiff base ligands derived from the condensation of the above mentioned diamine, salicylaldehyde derivatives and VO(acac)₂ with a template method. The electrochemical properties of the complexes were studied by means of cyclic voltammetry which shows the increase in the V^{IV}/V^V redox potential by the presence of electronegative groups. The crystal structures of the tridentate ligand (HL²) and the tetradentate oxidovanadium(IV) were also determined. The tetradentate complexes were used as catalysts for the oxidation of cyclooctene using tert-butylhydroperoxide and hydrogenperoxide as oxidant.

2. Experimental

2.1. Reagents and measurements

All chemicals were of the highest purity and were used as received. Cyclooctene and cycloocteneoxide were purchased from Aldrich and other chemicals were purchased from Merck. All the synthesis and purifications were conducted in aerobic condition. 4,5-Di-nitroorthophenylenediamine was synthesized following the literature procedure [22]. Melting points were obtained by a thermoscientific 9100 apparatus. ¹H NMR spectra were recorded



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on a 500 MHz Bruker FT-NMR spectrometer using CDCl₃ and DMSO- d_6 solvents; chemical shifts (δ) are given in ppm. IR spectra were obtained as KBr plates using a Bruker FT-IR instrument and UV–Vis spectra were obtained on a Shimadzu UV-1650PC spectro-photometer. Elemental analysis (C, H, N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analysesysteme, Gmbh, West Germany). A Metrohm 757 VA computerace instrument was employed to obtain cyclic voltammograms in acetonitrile at room temperature (25 °C) using 0.1 M tetra-*n*-butylammonium hexafluorophosphate solution as supporting electrolyte .GC analyses were carried out by a GC-17A Shimadzu instrument.

2.2. Synthesis of the tridentate ligands

2.2.1. Synthesis of N-salicylidene-4,5-dinitro-1,2-phenylenediamine (HL^1)

In a round-bottom two necked flask equipped with a reflux condenser, a magnetic stirrer and a dropping funnel, 0.4 g of 4,5-dinitro-o-phenylenediamine (2 mmol) was dissolved in 40 mL of absolute ethanol and was stirred and heated to the boiling point. After 10 min, a solution of 0.2 mL of 2-hydroxybenzaldehyde (2 mmol) in 20 mL of absolute ethanol was added drop-wise from the dropping funnel during approximately 20 min and the resulting yellow solution was stirred and refluxed for a further 60 min. The resulting dark orange solid was recrystallized from absolute ethanol and the crystalline target material was collected by suction filtration, washed successively with cold ethanol and diethyl ether and then air dried. M.p. 222 °C and the yield was 71%. Anal. Calc. for C₁₃H₁₀N₄O₅: C, 51.65; H, 3.31; N, 18.54. Found: C, 51.39; H,3.40; N, 18.83%. Selected IR data (v/cm^{-1} KBr): 3392, 3500 (v_{N-H}); 1629 $(v_{C=N})$. ¹H NMR (500 MHz, DMSO- d_6): 11.40 (1H, br, OH); 8.97 (1H, s, CH=N); 7.94 (1H, s, H_{Ar}); 7.87 (1H, d, H_{Ar}), 7.44 (1H, m, H_{Ar}); 7.13 (3H, br, H_{Ar} and NH₂); 6.99 (2H, m, H_{Ar}).

2.2.2. Synthesis of N-(4-methoxysalicylidene)-4,5-dinitro-1,2-phenylenediamine (HL²)

This compound was prepared following the same procedure as HL¹ except 4-methoxy-2-hydroxybenzaldehyde was used instead of salicylaldehyde. M.p. 210 °C and the yield was 77%. The product was recrystallized by slow evaporation of its solution in a mixture of chloroform/ethyl CH₃CN/Water (1:4 v/v) at room temperature and yellow crystals of HL² suitable for X-ray crystallography were obtained after two weeks. *Anal.* Calc. for C₁₄H₁₂N₄O₆: C, 50.60; H, 3.61; N, 16.87. Found: C, 50.44; H, 3.71; N, 16.55%. Selected IR data (ν /cm⁻¹ KBr): 3396, 3496 (ν _{N-H}); 1622 (ν _{C=N}). ¹H NMR (500 MHz, DMSO-*d*₆): 11.85 (1H, br, OH); 8.87 (1H, s, CH=N); 7.90 (1H, s, H_A_r); 7.73 (1H, d, H_A_r).

2.2.3. Synthesis of N-(3-methoxysalicylidene)-4,5-dinitro-1,2-phenylenediamine (HL³)

This compound was prepared following the same procedure as HL^1 except 3-methoxy-2-hydroxybenzaldehyde was used instead of Salicylaldehyde. The target compound was obtained as a yellow crystalline material. M.p. 234 °C and the yield was 71%. *Anal.* Calc. for $C_{14}H_{12}N_4O_6$: C, 50.60; H, 3.61; N, 16.87. Found: C, 50.61; H,3.32; N, 16.52%. Selected IR data (ν/cm^{-1} KBr): 3494, 3346 (ν_{N-H}); 1626 ($\nu_{C=N}$). ¹H NMR (500 MHz, DMSO- d_6): 11.28 (1H, br, OH); 8.98 (1H, s, CH=N); 7.96 (1H, s, H_{Ar}); 7.45 (1H, dd, H_{Ar}); 7.19 (1H, d, H_{Ar}); 7.13 (3H, br, H_{Ar} and NH₂); 6.94 (1H, m, H_{Ar}).

2.2.4. Synthesis of N-(5-bromosalicylidene)-4,5-dinitro-1,2-phenylenediamine (HL⁴)

This compound was prepared following the same procedure as HL¹ except 5-bromo-2-hydroxybenzaldehyde was used instead of Salicylaldehyde. The target compound was obtained as a yellow

crystalline material. M.p. 212 °C and the yield was 63%. *Anal.* Calc. for C₁₃H₉BrN₄O₅: C, 40.83; H, 2.36; N, 14.66. Found: C, 40.62; H,2.22; N, 14.14%. Selected IR data (ν /cm⁻¹ KBr): 3494, 3384 (ν _{N-H}); 1612 (ν _{C=N}). ¹H NMR (500 MHz, DMSO-*d*₆): 11.94 (1H, br, OH); 8.68 (1H, s, CH=N); 7.82 (1H, s, H_{Ar}); 7.67 (1H, d, H_{Ar}); 7.60 (1H, d, H_{Ar}); 7.03 (1H, s, H_{Ar}); 7.01 (1H, s, H_{Ar}); 4.96 (2H, br, NH₂).

2.3. Synthesis of tetradentate complexes

The complexes were synthesized by template method. The proper amounts of the diamine, the desired salicylaldehyde derivatives and VO(acac)₂ were mixed and refluxed in ethanol until the desired tetradentate complexes were precipitated.

2.3.1. Synthesis of {N,N'-bis(salicylaldiminato)}oxidovanadium(IV) VOLig¹.1.4 H₂O

0.2 g of 4,5-dinitro-o-phenylenediamine (1 mmol) and 0.2 mL 2-hydroxybenzaldehyde (2 mmol) were dissolved in 40 mL of absolute ethanol and the solution was stirred and heated to the boiling point in a two-necked round bottom flask equipped with a reflux condenser, a magnetic stirrer and a dropping funnel. From the dropping funnel was dripped a solution of 0.26 g (1 mmol) of bis(acetylacetonato)oxidovanadium(IV), (VO(acac)₂) in 40 mL of ethanol and then 1 mL of pyridine. A brown precipitate was obtained after 90 min which was collected by suction filtration and air dried. Recrystallization from acetonitrile yielded 31.3% of pure target complex. *Anal.* Calc. for C₂₀H_{14.8}N₄O_{8.4}V: C, 48.93; H, 3.02; N, 11.42. Found: C, 48.74; H, 3.18; N, 11.04%. Selected IR data (ν / cm⁻¹ KBr): 3416 (ν _{0-H}); 1609 (ν _{C=N}); 978 (ν _{V=O}). UV-Vis spectrum in CH₃CN [λ , nm, (ε , 1 mol⁻¹ cm⁻¹)]: 550(1146); 402(22 560); 323(34 246); 266(35 413).

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Crystal data, data	collection a	nd structure	refinement
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Compound	H_2L^2	VOLig ² ·DMF
Formula Formula weight	C ₁₄ H ₁₂ N ₄ O ₆ 332.28	C ₂₅ H ₂₃ N ₅ O ₁₀ V 604.42
Crystal system	triclinic	monoclinic
Space group	ΡĪ	$P2_1/n$
a (Å)	7.709(2)	13.447(2)
b (Å)	8.351(2)	16.376(2)
<i>c</i> (Å)	11.699(3)	24.025(3)
α (°)	109.56(1)	90
β (°)	91.80(2)	92.56(2)
γ (°)	96.93(2)	90
V (Å ³)	702.4(3)	5285.2(12)
Ζ	2	8
$D_x (g cm^{-3})$	1.571	1.519
F(000)	344	2488
μ (mm ⁻¹)	1.077	3.734
Θ range (°)	4.0-73.1	3.3-71.9
hkl range	$-9 \leqslant h \leqslant 9$	$-15 \leqslant h \leqslant 16$
	$-10 \leqslant k \leqslant 10$	$-18 \leqslant k \leqslant 20$
	$-14 \leqslant l \leqslant 14$	$-29 \leqslant l \leqslant 27$
Reflections		
Collected	11 927	21 738
Unique (Real)	2771(0.042)	10 223(0 027)
With $I > 2\sigma(I)$	2402	8901
Number of parameters	265	740
Number of parameters	205	740
Weighting scheme		
Α	0.0874	0.0500
В	0.1297	14.8459
Final R index $[I > 2\sigma(I)]$	$R_1 = 0.045$,	$R_1 = 0.081$,
	$wR_2 = 0.1305$	$wR_2 = 0.212$
R index [all data]	$R_1 = 0.050,$	$R_1 = 0.088,$
	$wR_2 = 0.136$	$wR_2 = 0.216$
Goodness-of-fit (GOF) on F^2	1.01	1.211
Maximum/minimum Δho (e Å $^{-3}$)	0.19/-0.27	0.74/-0.61



Fig. 1. Perspective view of HL² with labeling scheme. Displacement ellipsoids are drawn at 50% probability level; hydrogen atoms are depicted as spheres of arbitrary radii. Intramolecular hydrogen bond is shown as dashed line.



Scheme 1. The procedure of the synthesis of the ligands and complexes.

2.3.2. {N,N'-Bis(4-methoxysalicylaldiminato)}oxidovanadium(IV) VOLig²·DMF

This complex was prepared following the same procedure as described for VOLig¹ except 4-methoxy-2-hydroxybenzaldehyde was used instead of 2-hydroxybenzaldehyde. 35% of the pure target complex was obtained which was collected and recrystallized from DMF. Crystals suitable for X-ray crystallography were deposited after one week which were collected and air dried. *Anal.* Calc. for C₂₅H₂₃N₅O₁₀V: C, 49.63; H, 3.80; N, 11.58. Found: C, 49.94; H, 3.48; N, 11.42%. Selected IR data (ν /cm⁻¹ KBr): 1609 (ν _{C=N}); 978 (ν _{V=0}). UV–Vis spectrum in CH₃CN [λ , nm, (ε , 1 mol⁻¹ cm⁻¹)]: 480(1195); 411(31 480); 345(23 117); 211(35 227).

2.3.3. {N,N-Bis(3-methoxysalicylaldiminato)}oxidovanadium(IV) VOLig³·H₂O

This complex was prepared following the same procedure as described for VOLig¹ except 3-methoxy-2-hydroxybenzaldehyde was used instead of 2-hydroxybenzaldehyde. 33.4% of the target

complex was obtained as brown powder. *Anal.* Calc. for $C_{22}H_{18}N_4O_{10}V$: C, 48.08; H, 3.28; N, 10.20. Found: C, 48.56; H,3.54; N, 10.80%. Selected IR data (ν/cm^{-1} KBr): 3420 (ν_{O-H}); 1616 ($\nu_{C=N}$); 831($\nu_{V=0}$). UV–Vis spectrum in CH₃CN [λ , nm, (ϵ , 1 mol⁻¹ cm⁻¹)]: 570(1546); 436(7026); 318(17 720); 257(22 093).

2.3.4. {N,N'-Bis(5-bromoysalicylaldiminato)}oxidovanadium(IV) VOLig⁴·H₂O

This complex was prepared following the same procedure as described for VOLig¹ except 5-bromo-2-hydroxybenzaldehyde was used instead of 2-hydroxybenzaldehyde. 39.1% of the target complex was obtained as a brown powder. *Anal.* Calc. for C₂₀H₁₂Br₂N₄O₈V: C, 37.10; H, 1.85; N, 8.65. Found: C, 37.55; H,1.59; N, 8.90%. Selected IR data (ν /cm⁻¹ KBr): 3418 (ν _{O-H});1598 (ν _{C=N}); 877(ν _{V=O}). UV–Vis spectrum in CH₃CN [λ , nm, (ε , 1 mol⁻¹ cm⁻¹)]: 520(8200); 379(21 360); 332(23 360); 283(27 800).

Table	2
IdDIC	4

Selected geometrical parameters.

(VOLig ²) ₂ ·2DMF Bond lengths (Å)			
V1A-01A V1A-010A V1A-018A V1A-N7A V1A-N75A	1.586(4) 1.930(3) 1.931(4) 2.055(4) 2.060(4)	V1B-O1B V1B-O10B V1B-O18B V1B-N7B V1B-N15B	1.594(4) 1.935(3) 1.928(4) 2.059(4) 2.057(4)
Bond angles (°) N7A-V1A-N15A O18A-V1A-N15A O10A-V1A-018A O1A-V1A-N7A O1A-V1A-O10A O1A-V1A-O18A O1A-V1A-N7A O1A-V1A-N75A	78.04(17) 87.46(17) 86.75(15) 87.10(16) 108.45(18) 108.63(18) 105.9(2) 106.61(19)	N7B-V1B-N15B O18B-V1B-N15B O1B-V1B-O18B O1B-V1B-018B O1B-V1B-010B O1B-V1B-010B O1B-V1B-N7B O1B-V1B-N7B O1B-V1B-N15B	78.54(17) 87.31(17) 109.57(18) 106.1(2) 108.07(17) 109.57(18) 106.1(2) 104.35(19)
HL ² Bond lengths (Å) O10–C10 C8–C9 C8–N7 C10=C9	1.3488(18) 1.443(2) 1.2848(19) 1.410(2)		

Table	3
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Hydrogen bonds geometry (Å, °) in HL².

$D{-}H{\cdots}A$	D-H	$H{\cdots}A$	$D{\cdots}A$	DHA
010-H10· · ·N7	0.87(2)	1.83(3)	2.6158(18)	149(2)
N2−H22···051 ⁱ	0.85(2)	2.40(2)	3.138(3)	146(2)
N2-H22···N7	0.85(2)	2.40(2)	2.737(2)	103.9(19)
C6-H6···052	0.930(18)	2.363(18)	2.710(2)	101.8(13)
C8–H8· · ·O52 ⁱⁱ	0.963(19)	2.58(2)	3.544(2)	176.4(15)
$C11-H11\cdots O10^{iii}$	1.002(17)	2.473(17)	3.475(2)	178.3(13)

Symmetry codes: (i) x, 1 + y, z; (ii) -x, -y, 1 - z; (iii) 1 - x, 2 - y, 1 - z.

2.4. X-ray crystallography

Diffraction data were collected at room temperature by the ω -scan technique on an Oxford Diffraction SuperNova four-circle diffractometer with Atlas CCD detector, equipped with Nova microfocus Cu K α radiation source (λ = 5418 Å). The data were corrected for Lorentz-polarization as well as for absorption effects [23]. Precise unit-cell parameters were determined by a least-squares fit of 8226

(HL²) and 12 473 ([(VOLig²)]·DMF) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [24] and refined with the full-matrix least-squares procedure on F² by SHELXL97 [25]. The scattering factors incorporated in SHELXL97 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A.P)^2 + B.P]$ (P = [Max (F_o , 0) + $2F^2_c$]/3). The final values of A and B are listed in Table 1. All non-hydrogen atoms were refined anisotropically. In HL² hydrogen atoms were found in subsequent difference Fourier maps and freely refined with isotropic displacement parameters, in [VOLig²]·DMF the hydrogen atoms were placed geometrically in idealized positions and refined as rigid groups with their Uiso's as 1.2 or 1.5 (methyl) times Ueq of the appropriate carrier atom. Relevant crystal data are listed in Table 1, together with refinement details.

3. Results and discussions

3.1. Synthesis

The reaction between 4,5-dinitro-1,2-phenylenediamine and salicylaldehyde derivatives resulted in the condensation of only one of the NH_2 groups of the diamine even in the presence of two-fold excess of the aldehydes. This is most probably due to the precipitation of the half units in the reaction solvent. Besides, the crystal structure of HL^2 half unit (Fig. 1) clearly shows that the second NH_2 group remains coplanar with the aromatic ring, and this coplanarity makes the *para* amine be less reactive. Therefore, we decided to follow a template method to obtain the desired tetra-dentate Schiff base complexes.

3.2. Characterization of the ligands and complexes

The N₂O₂-type oxidovanadium(IV) Schiff base complexes that are used in this study and the tridentate ligands are shown in Scheme 1. The Schiff base ligands are characterized by elemental analyses, and ¹H NMR, IR and UV–Vis spectroscopy. The IR spectrum of the salicylaldehyde derivatives contains a band at around 1670 cm⁻¹ which is due to the presence of C=O group. In the IR spectra of the ligands, these bands have disappeared and are replaced with a new band at around 1620 cm⁻¹. This new band is due to the formation of azomethine group which shifts to lower wave numbers upon coordination to metal center. Furthermore,



Fig. 2. The crystal packing of HL² as seen along [0 0 1] direction. The dashed lines denote hydrogen bonds.



Fig. 3. Perspective view of one of the symmetry-independent pairs of VOLig².DMF with labeling scheme. Displacement ellipsoids are drawn at 50% probability level; hydrogen atoms are shown as spheres of arbitrary radii. C-H...O hydrogen bonds are drawn with dashed lines.

Table 4Hydrogen bonds geometry (Å, °) in $(VOLig^2)_2$ ·2DMF.

D−H···A	D-H	$H{\cdots}A$	$D{\cdots}A$	DHA
C2A−H2A···O1B ⁱ	0.93	2.52	3.360(6)	150
C2B–H2B· · ·O1A ⁱⁱ	0.93	2.42	3.101(6)	130
C8A–H8A· · ·O1B ⁱ	0.93	2.42	3.183(6)	139
C12C-H12G03C	0.96	2.47	2.842(11)	103
C12C–H12H·…O18A ⁱⁱ	0.96	2.6	3.439(10)	147
C12D–H12L···O18B ⁱⁱⁱ	0.96	2.52	3.331(10)	142
C5A−H5A···O3D ^{iv}	0.93	2.39	3.292(8)	164
C16A–H16A···O3D ^{iv}	0.93	2.31	3.176(7)	155
C5B−H5B····O3C ⁱⁱⁱ	0.93	2.36	3.284(9)	172
C16B−H16B···O3C ^v	0.93	2.33	3.241(8)	166

(i) -1 + x, y, 1 + z; (ii) 1 + x, y, -1 + z; (iii) -1/2 + x, 1/2 - y, 1/2 + z; (iv) -1 + x, y, z; (v) 1/2 + x, 1/2 - y, -1/2 + z.

the presence of two bands at around 3400 and 3500 cm⁻¹ is indicative of the presence of the amino group. These bands are also not present in the tetradentate complexes which support the condensation of both of the amino groups of the diamine. The ¹H NMR spectra of the tridentate ligands also contain signals at around 11 ppm due to the phenolic proton, 9 ppm due to the azomethine (HC=N) proton, and multiplets at around 7–9 ppm due to the aromatic protons. The broad signals due to amino group appear at around 7 ppm for HL¹⁻³ and 5 ppm for HL⁴. This downfield shift is most probably due to the non-coplanarity of the nitro group in the *para* position of this NH₂ group with the aromatic ring. The elemental analyses are also in agreement with the proposed structures.

3.3. Description of the crystal structures

Fig. 1 shows the perspective view of the tridentate ligand [HL²]. The crystal data for both structures are listed in Table 1, selected bond lengths are given in Table 2. The dihedral angle formed by the two phenyl rings is 16.12(7)°.The two nitro groups, due to the steric hindrance, are not coplanar with the parent benzene ring, and their planes make the dihedral angles with the mean

plane of the benzene ring of $14.82(18)^\circ$ and $80.5(3)^\circ$. The hydroxyl group is involved in an intramolecular $O-H\cdots N$ hydrogen bond which further stabilizes the almost coplanar disposition of the phenyl rings (Fig. 1, Table 3), The bond length pattern within the bridging C-C=N-C fragment reflects the delocalization of the electron density throughout this fragment: the formally single bonds are shorter and formally double bonds are longer than the typical values [26]. These patterns can be also related to a resonance-assisted hydrogen bond (RAHB) acting between molecules with conjugated multiple π bonds [27]. In the crystal structure the ligand molecules are connected into infinite chains along the *c* axis by intermolecular and intramolecular hydrogen bond (Fig. 2, Table 3).

The perspective view of the molecular structure of (VO-Lig²)₂·2DMF is shown in Fig. 3. The asymmetric unit consists of two crystallographically independent, but chemically identical and geometrically very similar complexes that however show some differences in their environment, particularly with respect to DMF molecules. The tetradentate Schiff base ligand (ONNO ligand) coordinates the vanadyl atom in four equatorial positions, and the terminal O atom occupies the axial position. The coordination geometry around V atoms approaches the distorted square pyramid. The bond angles in the basal plane of the complex, are all smaller than the ideal angle of 90° whereas the vertex angles are larger than 90° as a result of the central vanadium(IV) ion deviating from the basal plane towards the axial ligand (Table 2). In the structure of VOLig², the vanadium atoms are located 0.596(2) and 0.585(2) Å, in two symmetry-independent molecules, above the mean basal planes. These distances are quite similar to those observed for [VO(4-OH-salophen)] (0.600(2)Å) and [VO(3,5-tBu₂salophen)] (0.611 Å) [28,29]. The average V–N and V–O bond distances of the complex are similar to the current 73 vanadyl salen complexes in the Cambridge Structural Database ([30], given in square brackets): V-N bonds of 2.058(4) Å [2.07 Å], V-O bonds of 1.931(4) Å [1.88 Å], and a V=O bond of 1.590(4) Å [1.60 Å]. The DMF solvent molecule in complex is also anchored by relatively very short and linear C-H-··O hydrogen bonds (cf. Table 4). In the crystal structure, the complexes are connected into infinite chains along the c axis by intermolecular hydrogen bond (Fig. 4, Table 4).



Fig. 4. The crystal packing of (VOLig²)₂·2DMF as seen along [1 0 0] direction. The dashed lines denote hydrogen bonds.

3.4. Electrochemistry

The electrochemical behavior of the 10^{-3} M solutions of the tetradentate oxidovanadium(IV) Schiff base complexes were studied by means of cyclic voltammetry in DMSO solutions containing 0.1 M tetra-*n*-butylammoniumhexafluorophosphate (TBAHPF) as supporting electrolyte. Fig. 5 shows the voltammogram of the VO-Lig² and other voltammetry data are collected in Table 5. These data are consistent with the quasi-reversible V^{IV}/V^V redox process. The reported redox potential for the parent salophen VO(IV) complex is equal to 620 mV [31] which is shifted to 665 mV for VOLig¹, due to the NO₂ substitutions, and to 755 mV for VOLig⁴, due to both NO₂ and Br substitutions.

3.5. Catalytic studies

The oxidovanadium complexes were used as catalysts for the oxidation of cyclooctene using TBHP and H_2O_2 as oxidant in different solvents and various reaction conditions. The reaction progress was monitored by means of GC in 30 min intervals. In the absence of the catalyst complexes, no or very little oxidation products were observed. Oxidation of cyclooctene gave cycloocteneoxide as the sole product of the reaction. The retention times for the starting materials and the products were determined by means of the comparison with authentic samples. The conversion percent (%C) and the turn over numbers (T.N.) were calculated by the following equations in which C_{initial} and C_{final} are initial and final concentration of the substrate, respectively and [Q] is the concentration of the catalyst.

$$\% C = 100 \times \frac{C_{initial} - C_{final}}{C_{initial}}; \quad T.N. = \frac{\% Conversion \times C_{initial}}{[Q]}$$

In a typical experiment, 20 µmol of the catalyst, VOLig^{*n*}, was dissolved in 20 mL of freshly distilled acetonitrile and then 0.015 mol of cyclooctene and 0.03 mol of TBHP was added. The reaction mixture was refluxed while being stirred and the reaction progress was monitored at 30 min intervals. Various reaction



Fig. 5. Cyclic voltammogram of 10^{-3} M solution of VOLig² in DMSO containing 0.1 M TBAHFP and scan rate 50 mV s⁻¹.

Table 5

Cyclic voltammetry data of oxidovanadium(IV) complexes in DMSO solution containing 0.1 M tetra-*n*-butylammoniumhexafluorophosphate as supporting electrolyte.

Complex E_p^a (mV) E_p^c (mV) $E_{\frac{1}{2}}$ (mV) ΔE_p (mV) VOLig ¹ 620 710 665 90 VOLig ² 610 690 640 80 VOLig ³ 590 680 635 90 VOLig ⁴ 710 800 755 90	-				
VOLig ¹ 620 710 665 90 VOLig ² 610 690 640 80 VOLig ³ 590 680 635 90 VOLig ⁴ 710 800 755 90	Complex	E_p^a (mV)	E_p^c (mV)	$E_{\frac{1}{2}}$ (mV)	$\Delta E_{\rm P} ({ m mV})$
VOLIG 710 000 755 50	VOLig ¹ VOLig ² VOLig ³ VOLig ⁴	620 610 590 710	710 690 680 800	665 640 635 755	90 80 90 90

conditions were optimized. The optimized reaction time was obtained by following the reaction progress at 30 min intervals up to 10 and 6 h was found to be the optimized reaction time. The reaction was performed in acetonitrile at different reaction temperatures ranging from 50 to 80 °C (10 °C intervals) and 80 °C was found to be the optimized reaction temperature. The amounts of the catalysts were also optimized to 15 µmol and the oxidant to substrate ratio was also optimized to 2:1. TBHP was also found to

Table 6	
Oxidation of cyclooctene with	TBHP catalyzed by VO(IV) complexes in CH ₃ CN.



Solvent: 20 mL; catalyst: 15 µmol; duration: 6 h, at reflux; cyclooctene: 2 mL; TBHP: 4.12 mL.

Table 7 Oxidation of cyclooctene with H₂O₂ catalyzed by VO(IV) complexes in CH₃CN.

Complex	Conversion	Turnover	Products(%)
VOLig ¹	16	242	100
VOLig ²	11	166	100
VOLig ³	16	242	100
VOLig ⁴	12	182	100

Solvent: 20 mL; catalyst: 15 $\mu mol;$ duration: 6 h, at reflux; cyclooctene: 2 mL; TBHP: 4.12 mL.



Fig. 6. Plot of catalysts' activity for cyclooctene oxidation (T.N.) vs. V^{IV}/V^{V} reduction potential (mV) for VOLig^{*n*} (*n* = 1–4).

have better catalytic activity compared to H_2O_2 . Tables 6 and 7 show the results of the catalytic activity of the homogenous catalysts in optimized conditions. Fig. 6 shows the performance of the catalysts by comparison of the T.Ns. for the reaction of the epoxidation of cyclooctene with TBHP. As it could be seen, VOLig⁴ which has the more electronegative bromo group on the ancillary ligand system has greater E^0 and therefore, has greater Turnover numbers.

A good correlation between E^0 and turnover number could be seen from Fig. 6 for VOLig^{*n*} (*n* = 1, 2 and 4) but VOLig³, which has lower E^0 , shows greater catalytic activity compared to VOlig². This shows that other electronic and steric parameters would play important roles. In the case of VOLig³, the presence of methoxy groups close to the metal center may have special electronic effects such as hydrogen bonding and also steric effects. Therefore, more work is necessary to be done to fully understand the mechanism of the epoxidation reaction. Besides, a comparison with previous studies [31] which uses the oxidovanadium(IV) complex of salophen, with no substituents, for the epoxidation of olefins shows that the addition of two nitro groups to the diamine part of the ligand has increased both the E^0 and catalytic reactivity of the new catalysts.

4. Conclusion

We had previously shown that the presence of electronegative groups on the salicylaldehyde moiety of the Schiff base ligand system increases the E^0 of the V^{IV}/V^V couple and this increase in the redox potentials has a great influence on the catalytic efficiency of the oxidovanadium(IV) complexes. To further study the effect of electronegative groups on the catalytic efficiency of such complexes, we deliberately decided to prepare these new Schiff base derivatives in which two NO₂ groups present on the diamine part of the ligands. It is clear that the presence of these groups increases the catalytic ability of oxidovanadium(IV) complexes. In addition to the redox potentials, the fine structural details of the complexes would play an important role. The reactivity of the catalysts for the process of the oxidation of olefins seems to be a direct consequence of the electron-withdrawing substituents on the ligand skeleton.

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Appendix A. Supplementary data

CCDC 806592 and 806593 contains the supplementary crystallographic data for HL2 and VOLig2, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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