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Six-coordinated vanadium(IV) complexes with tridentate task-specific ionic liquid Schiff base ligands: Synthesis, characterization and effect of ionic nature on catalytic activity

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By reaction of 5-(chloromethyl)salicylaldehyde with triphenylphosphine and *N*-methylimidazole in two separate reactions, salicylaldehydetriphenylphosphonium chloride (S^2) and salicylaldehydemethylimidazolinium chloride (S^3) were prepared. Reaction of 2-(aminomethyl)pyridine with these aldehydes resulted in the task-specific ionic liquid Schiff base ligands L^1 and L^2, respectively. Then six-coordinated vanadium(IV) Schiff base complexes of VO(acac)L^{1-4} were synthesized by reactions of these tridentate Schiff base ligands and $VO(acac)_2$ in 1:1 stoichiometry. The aldehydes, ligands and VO(acac)L^{1-4} complexes were characterized using infrared, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, UV–visible and mass spectroscopies, as well as elemental analysis. Paramagnetic property of the complexes was also studied using magnetic susceptibility measurements. The complexes were used as catalysts in epoxidation of cyclooctene and oxidation of methylphenyl sulfide and the reaction parameters were optimized. The effect of the ionic nature of the complexes was investigated in these oxidation reactions. The catalytic activity of the complexes could be varied by changing the ionic (cationic or anionic) character of VO(acac)L^{1-4} catalysts in which counter anion variation showed a greater effect than cationic moiety variation.

KEYWORDS
ionic liquid, methylphenyl sulfide, oxidation reaction, Schiff base ligand, vanadium(IV) complex

1 | INTRODUCTION

The growing interest in recent years in the coordination chemistry of vanadium has been generated by the wide range of biological and catalytic properties of particular importance in the biosphere. Five- and six-coordinated vanadium complexes possessing potential medicinal applications, such as the treatment of diabetes type I and II[1] and preventive activity against carcinogenesis,[2] are only a few examples of vanadium complexes which can be found in nature. Moreover, Schiff base complexes can be widely employed as catalysts, e.g. in the stereoselective synthesis of cyclic ethers,[3] asymmetric alkynylation of aldehydes,[4] epoxidation of alkenes,[5] hydroxylation of phenols,[6] oxidation of bromides,[3] oxidative kinetic resolution of α-hydroxyesters[7] or the enantioselective

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oxidation of organic sulfides.[4,8] Optically active sulfoxides possess a wide range of biological activities, e.g. antimicrobial properties,[9] inhibition of biosynthesis of uric acid[10] and gastric acid secretion[11] or regulation of cholesterol catabolism.[12]

Ionic liquids have not only become increasingly popular as reaction and extraction media in research and development, but also they have widely been promoted as 'green solvents', which are regarded as powerful alternatives to volatile organic compounds in the field of organic synthesis. Furthermore, task-specific ionic liquids, where a functional group is covalently tethered to the cation or anion (or both) of the ionic liquid, are the latest generation of ionic liquids. The incorporation of this functionality should imbue an ionic liquid with a capacity to behave not only as a reaction medium but also as a reagent or catalyst in some reactions or processes.[13] Moreover, water-soluble ligands and their metal complexes containing ionic liquid fragments have emerged in the last decade as a synthetic strategy for homogeneous catalysis.

The investigation of the effect of the ionic nature of task-specific ionic liquid vanadyl Schiff base complexes is very rare. Therefore, in this paper, we describe the synthesis of task-specific ionic liquid Schiff base ligands and their vanadyl complexes, namely VO(acac)L^1, VO(acac)L^2, VO(acac)L^3 and VO(acac)L^4 (Scheme 1), and report an investigation of the catalytic activity of them in the epoxidation of cyclooctene and oxidation of methylphenyl sulfide as well as the effect of ionic nature in these reactions.

2 | EXPERIMENTAL

2.1 | Materials and techniques

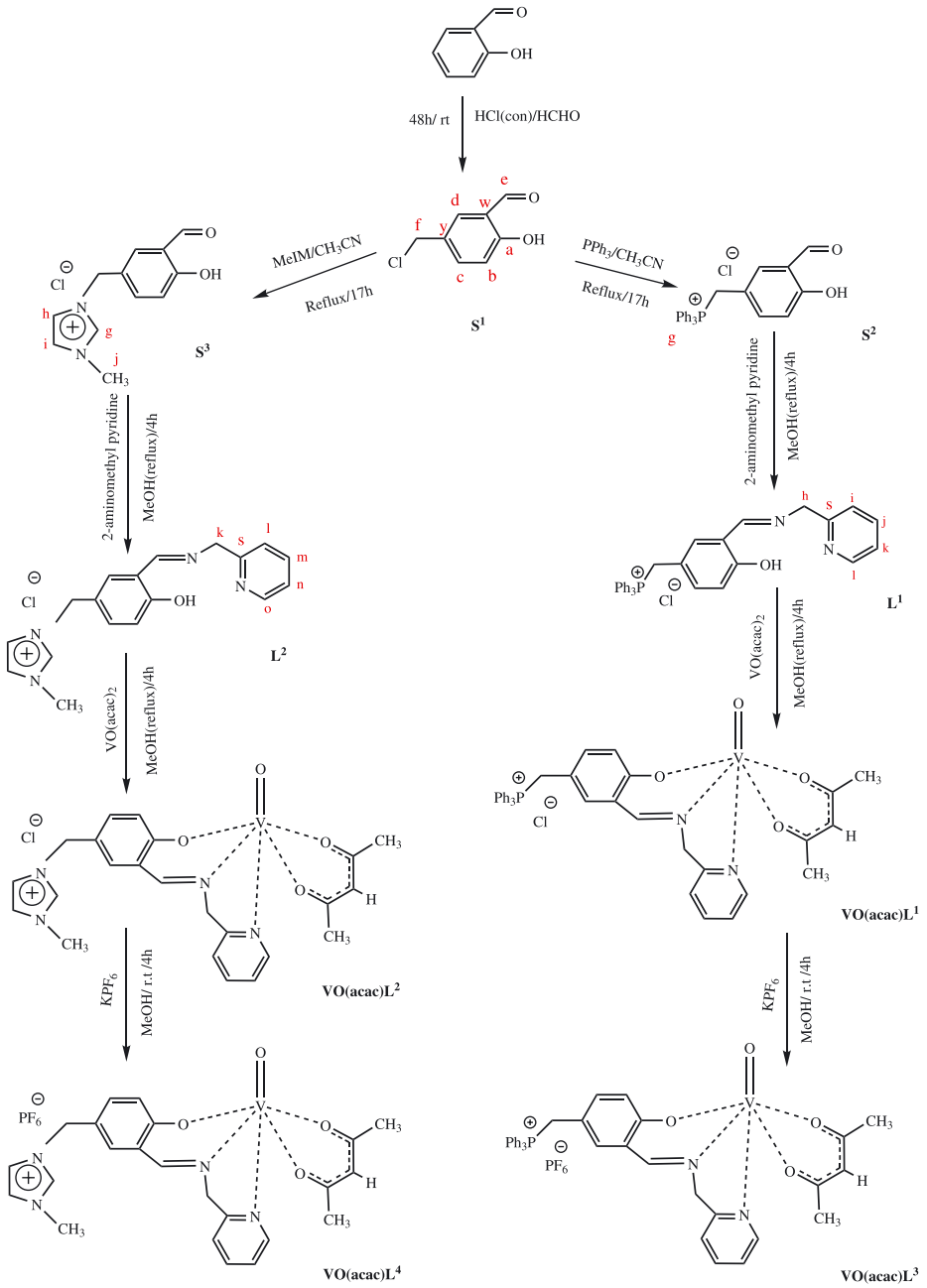
All reagents and solvents for synthesis and analysis were purchased from Merck and used as received without further purifications. *tert*-Butyl hydroperoxide (80%) in di-*tert*-butyl peroxide (TBHP) solution and 30% H_2O_2 solution from Merck were used in catalytic activity investigations. Infrared (IR) spectra were recorded in the range 400–4000 cm^{-1} with a PerkinElmer FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed with a Heraeus CHN–O-Rapid analyser and results agreed with calculated values. UV–visible spectra were recorded with a PerkinElmer Lambda 25 spectrometer. The NMR spectra of aldehydes and ligands were recorded with a Bruker 400 MHz spectrophotometer. The mass spectra of complexes were recorded with a Shimadzu spectrometer (GCMS-QP 1000 EX). Paramagnetic property of complexes was studied with a magnetic susceptibility balance (Sherwood Scientific). All GC yields based on the starting materials were obtained using a Varian CP-3800 instrument with a silicon-DC 200 column. All the ^{1}H NMR spectra of S^1, S^2, S^3, L^1 and L^2 and ^{31}P NMR spectra of S^2 and L^1 as well as ^{13}C NMR spectra of L^1 and L^2 are given in the supporting information.

2.2 | Synthesis of 5-(Chloromethyl) salicylaldehyde [$C_8H_7ClO_2$] (S^1)

Salicylaldehyde (15.25 g, 0.12 mol) and paraformaldehyde (2.25 g, 0.075 mol) were added to concentrated hydrochloric acid (100 ml) and the content stirred for 48 h at room temperature. After filtration, the white solid was washed five times with 1 M sodium hydrogen carbonate solution (each time with 70 ml) and dried under vacuum.[14] Yield: 10.85 g (51%). M.p. 84 °C. Anal. Calcd for ($C_8H_7ClO_2$) (%): C, 56.34; H, 4.10; N, 0. Found (%): C, 56.56; H, 4.07; N, 0. IR (KBr pellet, cm^{-1}): ν(O—H), 3340; ν(C—H)$_{aromatic}$, 2890–3010; ν(C—;H)$_{aliphatic}$, 2780–2870; ν(C—H)$_{aldehyde}$, 2784; ν(C═O), 1654; ν(C═C), 1483–1578; ν(C—O), 1192. ^{1}H NMR (δ, ppm; $CDCl_3$): 11.09 (1H, H^a); 7.03(1H, H^b); 7.52 (1H, H^c); 7.61 (1H, H^d); 9.90 (1H, H^e); 4.60 (2H, H^f).

2.3 | Synthesis of task-specific ionic liquids [$C_{26}H_{22}O_2P^+$]Cl^- (S^2) and [$C_{12}H_{13}O_2N_2^+$]Cl^- (S^3)

A solution of triphenylphosphine (1.53 g, 5.8 mmol) in dry acetonitrile (35 ml) was added to S^1 (1 g, 5.8 mmol). The solution was refluxed for 17 h. After filtration, light yellow solid of S^2 was obtained. Yield: 2.05 g (81%). M.p. 97 °C. Anal. Calcd for ($C_{26}H_{22}O_2P^+$)Cl^- (%): C, 72.15; H, 5.08. Found (%): C, 71.69; H, 4.74. IR (KBr pellet, cm^{-1}): ν(O—H), 3345; ν(C—H)$_{aromatic}$, 2990–3000; ν(C—H)$_{aliphatic}$, 2785–2870; ν(C—H)$_{aldehyde}$, 2690; ν(C═O), 1667; ν(C═C), 1434–1587; ν(C—O), 1151. ^{1}H NMR (δ, ppm; DMSO-d_6): 11.26 (1H, H^a); 7.03(1H, H^b); 7.05 (1H, H^c); 7.20 (1H, H^d); 10.15 (1H, H^e); 5.13–5.18 (2H, H^f); 7.64–7.76 (9H, $H^{g(3,4,5)}$); 7.86–7.90 (6H, $H^{g(2,6)}$). $^{31}P\{^1H\}$ NMR (δ, ppm; DMSO-d_6): 22.7. According to the above method, S^3 was obtained using 1-methylimidazole (0.47 g, 5.8 mmol) instead of triphenylphosphine. Yield: 1.39 g (94%). M.p. 101 °C. Anal. Calcd for ($C_{12}H_{13}O_2N_2^+$)Cl^- (%): C, 57.06; H, 5.14; N, 11.08. Found (%): C, 56.91; H, 4.87; N, 10.96. IR (KBr pellet, cm^{-1}): ν(O—;H), 3445; ν(C—H)$_{aromatic}$, 3048–3138; ν(C—;H)$_{aliphatic}$, 2705–2890; ν(C—H)$_{aldehyde}$, 2569; ν(C═O), 1674; ν(C═C), 1445–1613; ν(C—O), 1153. ^{1}H NMR (δ, ppm; $CDCl_3$): 11.43 (1H, H^a); 7.05 (1H, H^b); 7.11 (1H, H^c); 7.14 (1H, H^d); 9.98 (1H, H^e); 6.43 (2H, H^f); 8.05–8.06 (1H, H^g); 5.64 (1H, H^h); 7.61–7.66 (1H, H^i); 3.99–4.05 (3H, H^j).



SCHEME 1 Synthetic procedures for task-specific ionic liquid aldehydes S^{1-3}, Schiff base ligands $L^{1,2}$ and complexes VO(acac)L^{1-4}, and the labelling of protons and carbons in aldehydes and ligands

2.4 | Synthesis of task-specific ionic liquid Schiff Base ligands $[C_{32}H_{28}ON_2P^+]Cl^-.(2CH_3OH)$ (L^1) and $[C_{18}H_{19}ON_4^+]Cl^-.(2CH_3OH)$ (L^2)

Aldehyde S^2 (0.64 g, 1.48 mmol) was added to a solution of 2-(aminomethyl)pyridine (0.16 g, 1.48 mmol) in dry methanol (25 ml) and stirred for 4 h in reflux conditions. After evaporation of the solvent, an orange oily product of L^1 was obtained that was dried under vacuum for 24 h and a yellow film-like solid was obtained. Yield: 0.84 g (97%). M.p. 110 °C. Anal. Calcd for $(C_{32}H_{28}ON_2P^+)Cl^-.(2CH_3OH)$ (%): C, 69.67; H, 6.14; N, 4.78. Found (%): C, 69.92; H, 5.82; N, 5.15. IR (KBr pellet, cm^{-1}): $\nu(O—H)_{phenolic}$, 3344–3382; $\nu(C—H)_{aromatic}$, 3053; $\nu(C—H)_{aliphatic}$, 2858–2954; $\nu(C=N)$, 1635; $\nu(C=C)$ 1436–1587; $\nu(C—O)$, 1159. ^1H NMR (δ, ppm; DMSO-d_6): 13.39 (1H, H^a); 7.18 (1H, H^b); 7.23 (1H, H^c); 7.27 (1H, H^d); 8.42–8.44 (1H, H^e); 5.24–5.28 (2H, H^f); 7.52–7.67 (15H, H^g); 4.74 (2H, H^h); 6.78–6.81 (1H, H^i); 7.08–7.12 (1H, H^j); 6.52–6.55 (1H, H^k); 8.24 (1H, H^l). $^{13}C\{^1H\}$ NMR (δ, ppm; DMSO-d_6): 33.1 (C^f), 59.0 (C^h), 117.2 and 117.3 ($C^{g\text{-}Ipso}$), 118.3 (C^y), 119.7 (C^s), 122.2 (C^j), 122.5 (C^w), 129.9 (C^i), 130.1 (C^b), 130.2 (C^l), 133.9 (C^c), 134.1 (C^d), 134.7 ($C^{g\text{-}ortho\ or}$

meta), 134.8 ($C^{g\text{-ortho or meta}}$), 135.0 ($C^{g\text{-para}}$), 137.0 ($C^{k}$), 157.4 ($C^{a}$), 160.8 ($C^{e}$). $^{31}P\{^{1}H\}$ NMR (δ, ppm; DMSO-d_6): 22.6. UV–visible (nm): 269, 321. According to the above procedure, ligand L^2 was synthesized using S^3 (0.86 g, 3.4 mmol) instead of S^2 with 2-(aminomethyl)pyridine (0.37 g, 3.4 mmol). Yield: 1.32 g (96%). M.p. 122 °C. Anal. Calcd for $(C_{18}H_{19}ON_4^+)Cl^-.(2CH_3OH)$ (%): C, 59.04; H, 6.64; N, 13.77. Found (%): C, 58.98; H, 5.97; N, 14.12. IR (KBr pellet, cm^{-1}): $\nu(O—H)_{phenolic}$, 3844–3401; $\nu(C—H)_{aromatic}$, 3068; $\nu(C—H)_{aliphatic}$, 2843–2964; $\nu(C=N)$, 1637; $\nu(C=C)$ 1436–1590; $\nu(C—O)$, 1163. ^1H NMR (δ, ppm; DMSO-d_6): 13.50 (1H, H^a); 7.65 (1H, H^b); 7.72 (1H, H^c); 7.84 (1H, H^d); 9.35 (1H, H^e); 5.37 (2H, H^f); 8.72 (1H, H^g); 5.29 (1H, H^h); 8.16 (1H, H^i); 3.83–3.85 (3H, H^j); 4.91 (2H, H^k); 7.23–7.30 (1H, H^l); 7.38–7.44 (1H, H^m); 6.86–6.97 (1H, H^n); 8.52–8.54 (1H, H^o). $^{13}C\{^{1}H\}$ NMR (δ, ppm; DMSO-d_6): 35.8 (C^j), 48.8 (C^f), 51.8 (C^k), 118.2 (C^y), 119.6 (C^s), 120.6 (C^i), 121.6 (C^h), 121.9 (C^g), 122.0 (C^m), 123.7 (C^w), 123.8 (C^l), 125.5 (C^o), 132.1 (C^b), 135.6 (C^c), 136.2 (C^d), 136.4 (C^n), 157.5 (C^a), 167.8 (C^e). UV–visible (nm): 271, 319.

2.5 | Synthesis of task-specific ionic liquid Vanadyl Schiff Base complexes $[C_{37}H_{34}VO_4N_2P^+]Cl^-.(2CH_3OH.2H_2O)$ (VO(acac)L^1) and $[C_{23}H_{25}VO_4N_4^+]Cl^-.(2CH_3OH)$ (VO(acac)L^2)

$VO(acac)_2$ (0.4 g, 1.5 mmol) was dissolved in 35 ml of dry methanol. This solution was added to a solution of L^1 (0.79 g, 1.5 mmol) in 25 ml of methanol and the content was stirred for 4 h in reflux condition. By evaporation of solvent, a dark brown oily product of VO(acac)L^1 was obtained. After drying in a vacuum oven a greenish film-like solid was obtained. Yield: 0.98 g (93%). M.p. 207 °C. Anal. Calcd for $(C_{37}H_{34}VO_4N_2P^+)Cl^-.(2CH_3OH.2H_2O)$ (%): C, 60.82; H, 5.51; N, 3.83. Found (%): C, 60.53; H, 5.16; N, 4.04. IR (KBr pellet, cm^{-1}): $\nu(C—H)_{aromatic}$, 3311–3404; $\nu(C=H)_{aliphatic}$, 2810, 2958; $\nu(C=N)$, 1625; $\nu(C=C)$, 1519–1587; $\nu(C—O)$, 1164; $\nu(V=O)$, 946. Mass (m/z): 787 (M^+), 786, 683, 262, 183, 166, 152, 107, 92, 77, 63, 49, 43 (M^+). UV–visible (nm): 271, 380, 550 (d–d). Complex VO(acac)L^2 was synthesized according to the above procedure by the reaction between L^2 (1.17 g, 3.4 mmol) and $VO(acac)_2$ (0.91 g, 3.4 mmol). Yield: 1.49 g (91%). M.p. 157 °C. Anal. Calcd for $(C_{23}H_{25}VO_4N_4^+)Cl^-.(2CH_3OH)$ (%): C, 52.50; H, 5.77; N, 9.80. Found (%): C, 51.83; H, 5.41; N, 9.16. IR (KBr pellet, cm^{-1}): $\nu(C—H)_{aromatic}$, 3078–3390; $\nu(C–H)_{aliphatic}$, 2832, 2950; $\nu(C=N)$, 1634; $\nu(C=C)$, 1314–1592; $\nu(C—O)$, 1163; $\nu(V=O)$, 947. Mass (m/z): 571 (M^+), 388, 345, 265, 249, 183, 166, 158, 100, 92, 85, 82, 67, 43 (M^+). UV–visible (nm): 271, 381, 552 (d–d).

2.6 | Synthesis of task-specific ionic liquid Vanadyl Schiff Base complexes $[C_{37}H_{34}VO_4N_2P^+]PF_6^-$ (VO(acac)L^3) and $[C_{23}H_{25}VO_4N_4^+]PF_6^-$ (VO(acac)L^4)

Anion exchange was carried out at room temperature in water solution, between anions of Cl^- and PF_6^- for these complexes. The reaction of 1:1 solutions of VO(acac)L^1 (0.51 g, 0.65 mmol) and potassium hexafluorophosphate (0.12 g, 0.65 mmol) resulted in synthesis of complex VO(acac)L^3. Yield: 0.44 g (86%). M.p. 190 °C. Anal. Calcd for $(C_{37}H_{34}VO_4N_2P^+)PF_6^-$ (%): C, 55.07; H, 4.26; N, 3.51. Found (%): C, 54.44; H, 4.01; N, 3.86. IR (KBr pellet, cm^{-1}): $\nu(C—H)_{aromatic}$, 3064–3317; $\nu(C—H)_{aliphatic}$, 2921, 2983; $\nu(C=N)$, 1635; $\nu(C=C)$, 1471–1598; $\nu(C—O)$, 1163; $\nu(V=O)$, 951. Mass (m/z): 796 (M^+), 410, 262, 230, 183, 115, 105, 89, 77, 63, 49 (M^+). UV–visible (nm): 271, 382, 549 (d–d). According to the above method, the anion exchange for complex VO(acac)L^2 was carried out in 1:1 solutions of VO(acac)L^2 (0.52 g, 0.91 mmol) and potassium hexafluorophosphate (0.17 g, 0.91 mmol) resulting in the synthesis of complex VO(acac)L^4. Yield: 0.47 g (84%). M.p. 218 °C. Anal. Calcd for $(C_{23}H_{25}VO_4N_4^+)PF_6^-$ (%): C, 44.5; H, 4.03; N, 9.03. Found (%): C, 45.01; H, 3.84; N, 9.16. IR (KBr pellet, cm^{-1}): $\nu(C—H)_{aromatic}$, 3157; $\nu(C—H)_{aliphatic}$, 2917; $\nu(C=N)$, 1633; $\nu(C=C)$,1473–1593; $\nu(C—O)$, 1163; $\nu(V=O)$, 948. Mass (m/z): 616 (M^+), 615, 328, 286, 191, 164, 100, 92, 85, 82, 67, 43 (M^+). UV–visible (nm): 271, 381, 551 (d–d).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

S^1 was prepared as described previously.[14] Then by reaction of S^1 with triphenylphosphine and methylimidazole, the task-specific ionic liquids S^2 and S^3 were synthesized, respectively. After synthesis of Schiff base ligands L^1 and L^2, the reactions of them with $VO(acac)_2$ resulted in the task-specific ionic liquid vanadyl Schiff base complexes VO(acac)$L^{1,2}$. Then the anion exchange of Cl^- by PF_6^- carried out for VO(acac)$L^{1,2}$ led to synthesis of complexes VO(acac)$L^{3,4}$. Also, the solubility of the task-specific ionic liquid Schiff base ligands and their complexes was investigated in various organic solvents and water. They are soluble in most of solvents, especially in water. The synthetic procedures are shown in Scheme 1.

3.2 | IR spectra

The IR spectra of S^1, S^2 and S^3 show absorptions at 3340, 3345 and 3445 cm^{-1}, which are related to O—H bonds

and also show absorptions at 1654, 1667 and 1674 cm^{-1} for the C═O bonds. Broad bands at 3344–3382 and 3384–3401 cm^{-1} in the IR spectra of ligands L^1 and L^2 can be related to O—H of phenol and CH_3OH. A similar broad band is seen in the IR spectra of VO(acac)$L^{1,2}$ related to O—H of CH_3OH and/or H_2O which is not seen in the IR spectra of complexes VO(acac)$L^{3,4}$. The fundamental stretching mode of the azomethine moiety $\nu_{C=N}$ for the free ligands L^1 and L^2 appears at 1635 and 1637 cm^{-1}, respectively, which shifts to lower frequencies and seen at 1625, 1634, 1635 and 1633 cm^{-1} in the IR spectra of VO(acac)L^{1-4}. These changes are attributed to the coordination of nitrogen in azomethine of ligands to the V(IV) centre. As is generally seen, complexes VO(acac)L^{1-4} showed $\nu_{V=O}$ at around 946, 947, 951 and 948 cm^{-1} as monomeric vanadyl Schiff base complexes.[15,16]

3.3 | NMR spectra

The obtained ^1H NMR spectra of VO(acac)L^{1-4} did not give useful information because of their paramagnetic properties. But the ^1H NMR spectra of S^1, S^2, S^3, L^1 and L^2 were obtained. The proton labelling of S^1, S^2, S^3, L^1 and L^2 is given in Scheme 1. The chemical shifts for S^1 at 11.09, 7.03, 7.52 and 7.61 ppm were seen for H^a, H^b, H^c and H^d protons of salicylate moiety. These resonances for S^2 appeared at 11.26, 7.03, 7.05, 7.20 ppm and for S^3 at 11.43, 7.05, 7.11, 7.14 ppm. The resonances at 9.90, 10.15 and 9.98 ppm corresponded to H^e in S^1, S^2 and S^3, respectively, and proton signals of methylene group also appeared at 4.60, 5.13–5.18 and 6.43 ppm related to H^f in S^1, S^2 and S^3. The proton signals of $H^{g(3,4,5)}$ from phenyl group of triphenylphosphonium moiety in S^2 were seen at 7.64–7.76 ppm and other proton signals of $H^{g(2,6)}$ were observed at 7.86–7.90 ppm. In addition, the proton signals of H^g for S^3 were seen at 8.05–8.06 ppm and the signals at 5.64, 7.61–7.66 and 3.99–4.05 ppm are related to H^h, H^i and H^j of S^3, respectively. For ligands L^1 and L^2 in the downfield region of each spectrum, one singlet resonance appeared at 13.39 and 13.50 ppm, respectively, attributed to the phenolic proton of H^a. These signals were shifted downfield because of the formation of strong intramolecular hydrogen bonding between the phenolic proton and nitrogen of imine. Some other signals appeared at about 7.18, 7.23, 7.27 and 8.42–8.44 ppm corresponding to the aromatic protons of H^b, H^c, H^d and iminic proton H^e for L^1 and at 7.65, 7.72, 7.84 and 9.35 ppm for L^2, respectively. In addition, the resonance of H^f was observed at 5.24–5.28 and 5.37 ppm for L^1 and L^2 and the protons of aromatic rings of triphenylphosphonium showed signals in the region 7.52–7.67 ppm for L^1 and the resonance of H^g proton of imidazolinum moiety in L^2 appeared at 5.41 ppm. Some other resonances are seen at about 4.74, 6.78–6.81, 7.08–7.12, 6.52–6.55 and 8.42 ppm attributed to the protons of H^h, H^i, H^j, H^k and H^l for L^1 and at about 5.29, 8.16, 3.83–3.85, 4.91 and 7.23–7.30 ppm for L^2, respectively. Other signals are seen at about 7.38–7.44, 6.86–6.97 and 8.52–8.54 ppm related to the protons of H^m, H^n and H^o, respectively, for L^2.

The ^{13}C NMR spectra of L^1 showed chemical shifts at 33.1, 59.0, 118.3, 119.7, 122.2, 122.5, 129.9 and 130.2 ppm related to C^f, C^h, C^y, C^s, C^j, C^w, C^i and C^l, as well as signals of ($C^{g\text{-Ipso}}$), ($C^{g\text{-ortho or meta}}$) and ($C^{g\text{-para}}$) that appeared at 117.2, 134.7, 134.8 and 135.0 ppm, respectively. For salicylate moiety, resonances at 130.1, 133.9 and 134.1 ppm were seen for C^b, C^c and C^d, respectively, and other resonances at 137.0, 157.4 and 160.8 ppm are related to C^k, C^a and C^e. Also, for L^2 resonances at 35.8, 48.8, 51.8, 118.2, 119.6, 122.0, 123.7, 123.8 and 125.5 ppm are related to C^j, C^f, C^k, C^y, C^s, C^m, C^w, C^l and C^o, respectively, and the carbon signals of C^i, C^h and C^g appeared at 120.6, 121.6 and 121.9 ppm, as well as resonances at 132.1, 135.6 and 136.2 ppm corresponding to C^b, C^c and C^d. Other resonances at 136.4, 157.5 and 167.8 ppm are related to C^n, C^a and C^e, respectively.

In addition, the ^{31}P NMR spectra were recorded for S^2 and L^1. These showed a singlet resonance at 22.7 and 22.6 ppm for S^2 and L^1, respectively.

3.4 | UV–visible spectra

The UV–visible spectra of ligands and complexes are shown in Figure 1. The spectra of VO(acac)L^{1-4} were broader than those of free ligands of $L^{1,2}$ because of the coordination of anionic form of ligands (as phenolate) and resonance of charge in a longer route.[17] The UV–visible spectra of ligands in DMSO showed two bands at 269 and 321 nm for L^1 and two bands at 271 and 319 nm for L^2 due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. For VO(acac)L^{1-4}, these bands appeared at 271 and 380 nm for VO(acac)L^1, 271 and 381 nm for VO(acac)L^2, 271 and 382 nm for VO(acac)L^3 and finally 271 and 381 nm for VO(acac)L^4. In addition, very weak bands corresponding to d–d transitions appeared at 550, 552, 549 and 551 nm for VO(acac)L^{1-4}, respectively.

3.5 | Mass spectra

Mass spectrometric data for VO(acac)L^{1-4} are consistent with the structures proposed on the basis of other spectroscopic data. In some cases, the ion molecule shows very low intensity and in rare cases is not seen.[18] The mass spectrum of VO(acac)L^1 shows expected signals at m/z of 787 (M^+), 786, 683, 262, 183, 166, 152, 107, 92, 77, 63, 49 and 43. The molecular weight of complex [VO(acac)L^1].($2CH_3OH.2H_2O$) is 787 (M^+) that is not seen, but with loss

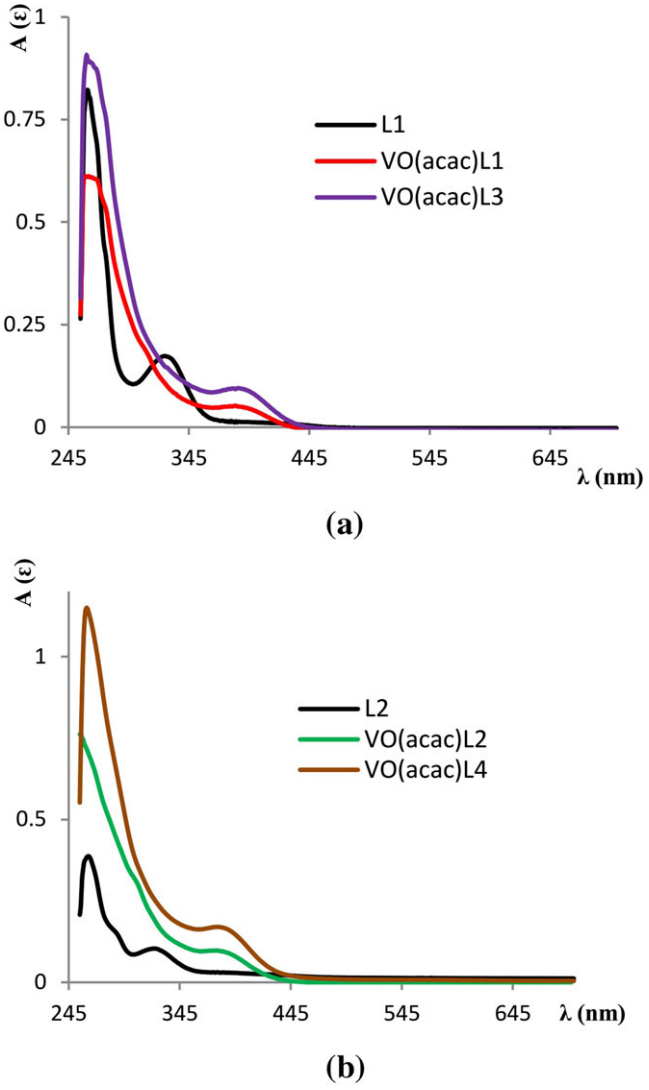


FIGURE 1 UV–visible spectra of (a) L^1 and VO(acac)$L^{1,3}$ and (b) L^2 and VO(acac)$L^{2,4}$ (10^{-4} M in DMSO)

of one hydrogen atom, a signal at *m/z* 786 is seen. The peak at *m/z* 683 is attributed to the residue of molecular weight by loss of $2CH_3OH$ and $2H_2O$ and also four hydrogen atoms. The base peak at *m/z* 43 is related to the $^+$PC fragment and other signals at *m/z* 262, 183, 166 and 152 are related to the $^+PPh_3$, $^+PPh_2$ and VO(acac) fragments and the ion produced from VO(acac) by loss of methyl group and then adding one hydrogen atom resulting in formula of $C_4H_6VO_3$. Signals at *m/z* 107 and 92 are attributed to the $^+$PPh and acac fragments with formula of $[C_5H_7O_2]$. Finally, the signal at *m/z* 77 is attributed to the phenyl group, and by loss of the first and second methylene groups, signals at *m/z* 63 and 49 appeared, respectively. The mass spectrum of complex VO(acac)L^1 is shown in Figure 2.

The mass spectrum of VO(acac)L^2 exhibits signals at *m/z* 571 (M^+), 388, 345, 265, 249, 183, 166, 158, 100, 92, 85, 82, 67 and 43. The peak at *m/z* 571 is assigned to the molecular weight of [VO(acac)L^2.$2CH_3OH$] and the base peak at *m/z* 85 is related to the loss of methyl group from acac fragment. The sharp peak at *m/z* 388 is related to the residue of molecular weight by loss of $2CH_3OH$ and $HCNCH_2Py$ fragment. Also, the peak at *m/z* 345 is due to the CIm^+—$CH_2C_6H_3OVO$(acac) fragment by loss of four hydrogens, with formula of $C_{16}H_{15}N_2VO_4^+$. The peaks at *m/z* 265 and 249 are related to the CIm^+—$CH_2C_6H_3VO_3$ and CIm^+—$CH_2C_6H_3VO_2$ fragments with formulas of $C_{11}H_7N_2VO_3$ and $C_{11}H_7N_2VO_2$, respectively. Other peaks at *m/z* 183, 166, 158 and 100 are attributable to CIm^+—$CH_2C_6H_3O$ with formula of $C_{11}H_8N_2O$, VO(acac), CH_2PyVO and acac that gained one hydrogen, respectively, and the signal at *m/z* 92 is related to CH_2Py. Also the signals at *m/z* 82 and 67 are due to methylimidazole and the loss of methyl group from it, with formulas of $C_4H_6N_2$ and $C_3H_3N_2$, respectively. Finally the peak at *m/z* 43 is related to the HN═CH—NH_2 fragment that resulted from decomposition of the imidazole part, with loss of one hydrogen.

Similarly, the mass spectra of complexes VO(acac)$L^{3,4}$ confirm their chemical composition. The mass spectrum of VO(acac)L^3 shows signals at *m/z* 796 (M^+), 410, 262, 230, 183, 115, 105, 89, 77, 63 and 49. The molecular weight of VO(acac)L^3 is represented by *m/z* 796, but this signal is not seen because of the instability of the ligand in the ion source of the mass spectrometer, but the molecular weight will be proven by the fragments in the mass spectrum. The signal at *m/z* 410 is related to the residue of molecular weight by loss of [$HCNCH_2Py$] and $^+PPh_3$ fragments and also loss of five hydrogens from the complex. The base peak at *m/z* 77 is attributed to the phenyl group and the signal at *m/z* 262 is related to $^+PPh_3$. Signals at *m/z* 230, 183 and 115 are attributed to the $CH_2C_6H_3(CHN)VO_4$, $^+PPh_2$ and $CH_2C_6H_3HC$═N fragments, respectively. Also the signals at *m/z* 105 and 89 are related to the $CH_2C_6H_3O$ and CH_2Py fragments by loss of three hydrogens. Finally, the signals at *m/z* 63 and 49 are attributed to the loss of first and second methylene groups from phenyl group, respectively.

The mass spectrum of VO(acac)L^4 exhibits peaks at *m/z* 616 (M^+), 615, 328, 286, 191, 164, 100, 92, 85, 82, 67 and 43. The molecular weight of VO(acac)L^4 is equal to 616 (M^+), the peak of which is not seen, but with loss of one hydrogen atom, the signal at *m/z* 615 is seen. Also the base peak at *m/z* 43 is related to the HN═CH—NH_2 fragment that results from decomposition of the imidazole part, with loss of one hydrogen. The signal at *m/z* 328 is attributed to the residue of molecular weight by loss of $HCNCH_2Py$ and VO(acac) fragments and also three hydrogen atoms from the complex. Signals at *m/z* 286 and 191 are related to the $HCNCH_2PyVO$(acac) and CH_2PyVO_3 fragments, respectively. Other peaks at *m/z* 164 and 100 are attributable to loss of two hydrogens from

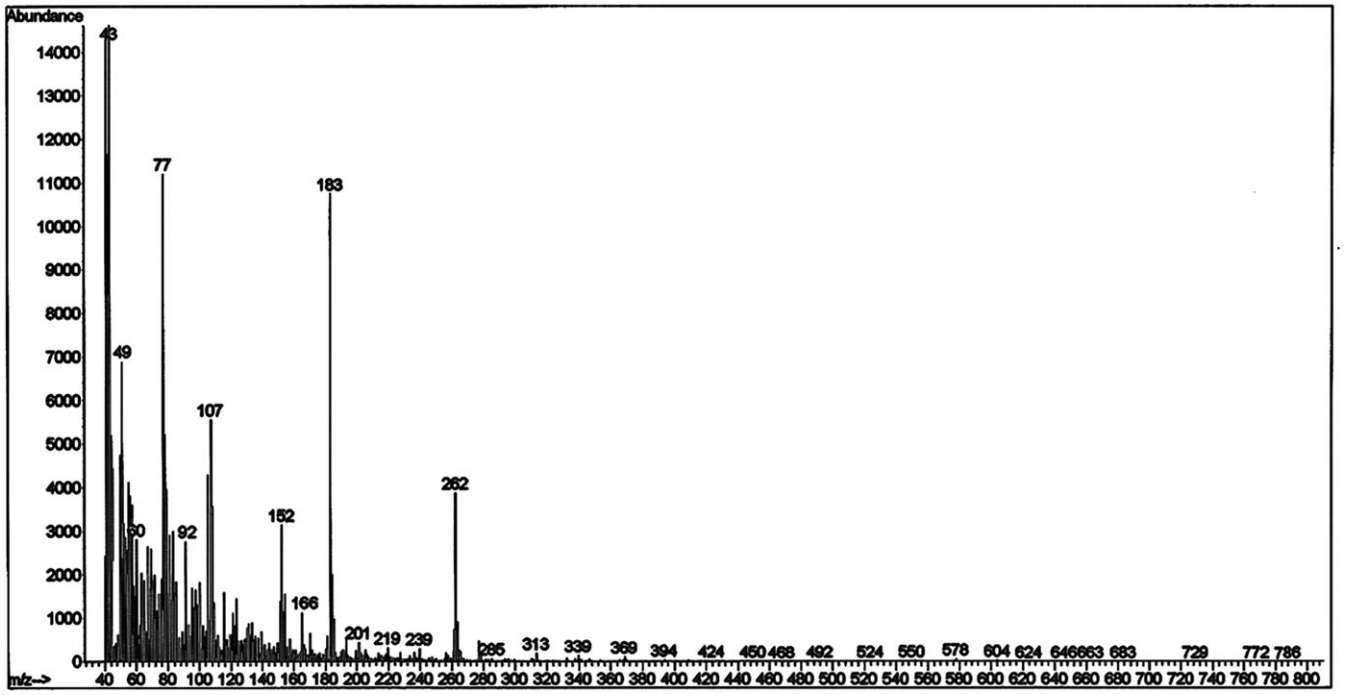


FIGURE 2 Mass spectrum of VO(acac)L^1 complex

VO(acac) and acac fragment that gained one hydrogen, respectively. Also the signal at m/z 92 is related to the CH_2Py fragment and that at m/z 85 is attributed to loss of methyl group from acac fragment. Finally the signals at m/z 82 and 67 are due to the methylimidazole fragment with formula $C_4H_6N_2$ and loss of the methyl group from it with formula $C_3H_3N_2$, respectively.[18]

3.6 | Magnetic properties

The total measured magnetic susceptibility (χ_{meas}) was determined using the equation $\chi_{meas} = \chi_g M_w$, in which χ_g is mass susceptibility, where $\chi_g = [C_{Bal}l(R - R_0)]/[(m - m_0) \times 10^9]$. On the other hand, χ_{meas} is defined as the sum of contributions: $\chi_{meas} = \chi_P + \chi_D$, where χ_D is diamagnetic correction made with Pascal's constants for all constituent atoms and χ_P is paramagnetic susceptibility. The latter can be related to the number of unpaired electrons in a complex and it is measured after determination of the value of χ_D using the equation $\chi_P = \chi_{meas} - \chi_D$. Then the magnetic moment was calculated using the equation $\mu_{eff} = 2.828(\chi_P T)^{1/2}$, where T is absolute temperature. This is equivalent to $\mu_{eff} = [n(n + 2)]^{1/2}$ (n = unpaired electrons) when the spin-only formula can be used which is usual for first row transition metals when the orbital contribution is largely quenched. Hence, if $\mu_{eff} = 1.73$, then $n = 1$. Matching of μ_{eff} to the nearest value to find n and comparison of this value with the theoretical one predicted knowing the element and its oxidation state such as the emphasis on vanadium in oxidation states +4 or +5.[19–21] As one-electron system of six-coordinated V(IV) complexes with $3d^1$ electron configuration and $S = 1/2$ possesses an orbitally nondegenerate ground state (^2B_2g), by the static Jahn–Teller distortion (z-in), partially quenched orbital contributions to the magnetic moment and also $g_{||}$ and $g_\perp$ are not substantially different from 2. Therefore, the g-values are close to 2. It is expected to obey Curie–Weiss behaviour with near or equal to zero and moments close to the spin-only value. In fact, the Curie law is followed with magnetic moments close to the spin-only value. The magnetic susceptibilities of the complexes VO(acac)L^{1-4} were measured at 292 K and the results are presented in Table 1. The low symmetry of complexes VO(acac)L^{1-4} removes the orbital degeneracy so the experimental magnetic moment values (μ_{eff})

TABLE 1 Measurements of magnetic susceptibilities (χ) and μ_{eff}

Complex (V^{4+}), ($3d^1$)	χ_g ($\times 10^{-7}$)	χ_{meas} ($\times 10^{-4}$)	χ_D ($\times 10^{-6}$)	χ_P ($\times 10^{-3}$)	μ_{eff} (exp.)	μ_{eff} (calc.) = $\mu_{spin\text{-}only}$
VO(acac) L^1	9.12)	7.186	−518.62	1.237	1.70	1.73
VO(acac) L^2	15.3	8.742	−333.37	1.207	1.67	1.73
VO(acac) L^3	1.36	1.090	−1122.36	1.231	1.69	1.73
VO(acac) L^4	3.58	2.208	−996.83	1.217	1.68	1.73

for paramagnetic vanadium complexes VO(acac)L^{1-4} at 292 K are very close to the spin-only value expected for one unpaired electron with $S = 1/2$ for uncoupled spin systems (1.73). Thus these measurements confirm the oxidation state of complexes VO(acac)L^{1-4}.[21]

3.7 | Catalytic activity

3.7.1 | Epoxidation of cyclooctene

In order to assess the catalytic activity of complexes VO(acac)L^{1-4} in epoxidation reactions, cyclooctene was used as a model substrate and various reaction parameters, such as solvent, oxidant, alkene/oxidant ratio and amount of catalyst, were optimized with complex VO(acac)L^1. Figure 3 illustrates the results of epoxidation of cyclooctene in the presence of TBHP as an oxidant with a catalytic amount of complex VO(acac)L^1 in various solvents. The trend of the observed solvent effect was $CHCl_3$ > CH_3CN–H_2O > $C_2H_4Cl_2$ > CCl_4 > CH_3CN > THF > CH_3OH > H_2O. The low conversion in THF, CH_3OH and H_2O can be related to the high coordination ability of these solvents to the metal centre. As the coordination ability of the solvent is increased, the activity of the complex is decreased.[22,23] Dielectric constant of solvent is another factor that could affect the catalytic activity. This trend can be given as:[24] H_2O (80.3) > CH_3CN (37.5) > CH_3OH (32.7) > $C_2H_4Cl_2$ (10.3) > THF (7.58) > $CHCl_3$ (4.9) > CCl_4 (2.2). It seems that in protic solvents with high polarity and high dielectric constant (H_2O and CH_3OH) the lowest catalytic activity is observed. High activity of the catalyst is observed in aprotic solvents with moderate dielectric constants. Among them, high conversion (89%) was observed in $CHCl_3$ with moderate dielectric constant and without any coordination ability to the metal centre.

We also investigated different reaction media to obtain a suitable oxidant for the epoxidation of cyclooctene

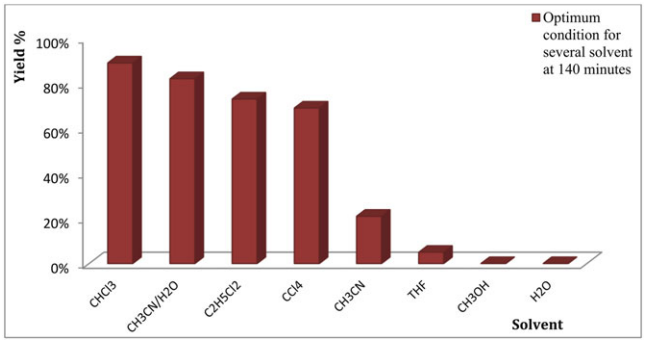


FIGURE 3 Effect of solvent on conversion of cyclooctene to cyclooctene epoxide under reflux conditions in the presence of TBHP as oxidant with catalytic amount of VO(acac)L^1 complex. (Reaction conditions: $CHCl_3$ as solvent, 5 ml; cyclooctene, 0.5 mmol; TBHP, 1.5 mmol; catalyst, 0.01 mmol)

(Table 2). The results show that the activity of the complex VO(acac)L^1 in the epoxidation of cyclooctene in the presence of TBHP in $CHCl_3$ is higher than in the presence of H_2O_2 and $NaIO_4$. This may be related to the ability of TBHP and the inability of H_2O_2 and $NaIO_4$ to mix with the organic substrate phase. In addition, we optimized the effect of cyclooctene/oxidant ratio (by using 1:1.2, 1:2, 1:3 and 1:4 ratios) and the effect of the catalyst amount (0.005, 0.01 and 0.02 mmol) in the epoxidation reaction of cyclooctene catalysed by complex VO(acac)L^1. According to these experiments, a cyclooctene/oxidant ratio of 1:3 and 0.01 mmol of catalyst can be chosen as optimal providing high epoxide yields. The results for other catalysts, VO(acac)L^{2-4}, under various conditions in the presence of different oxidants and substrate/oxidant ratio of 1:3, were obtained and are presented in Table 3.

In order to characterize the reaction products, in a typical reaction, after reaction completion under optimal conditions using VO(acac)L^1, the cyclooctene epoxide was isolated by column chromatography. After evaporation of the solvent and isolation the cyclooctene epoxide, it was characterized using ^{1}H NMR spectroscopy (see supporting information (F10) for the ^{1}H NMR spectrum of cyclooctene epoxide). Thus reactions catalysed by VO(acac)L^{2-4} were carried out under these optimum conditions. For VO(acac)L^1 in optimum conditions the yield was 89% in 140 min, whereas these yields when using VO(acac)L^2, VO(acac)L^3 and VO(acac)L^4 catalysts are 81, 89 and 45%, respectively, under optimum conditions (Figure 4). Thus the observed trend in catalytic activity of these catalysts in epoxidation of cyclooctene was: VO(acac)L^1 ~ VO(acac)L^3 > VO(acac)L^2 > VO(acac)L^4.

As seen from Scheme 1, the coordination spheres of these catalysts are the same and only the ionic pendant groups are different. Thus it seems that a change of the ionic part in these complexes would affect their catalytic activity. By changing the cationic part of the catalyst from triphenylphosphonium cation in VO(acac)L^1 to methylimidazolium cation in VO(acac)L^2 with constant anion of Cl^-, the catalytic activity was decreased. When the counter anion of Cl^- in VO(acac)L^1 was substituted

TABLE 2 Epoxidation of cyclooctene in presence of various oxidants under different conditions[a] catalysed by VO(acac)L^1

Solvent	Oxidant	Time (min)	Conversion (%)
$CHCl_3$	TBHP	140	89
$CHCl_3$	H_2O_2	140	2
$CHCl_3$	$NaIO_4$	140	12
CH_3CN–H_2O (3:2)	H_2O_2	140	No reaction
CH_3CN–H_2O (3:2)	$NaIO_4$	140	No reaction

[a]Reaction conditions: solvent: 5 ml; cyclooctene: 0.5 mmol; TBHP: 1.5 mmol; catalyst VO(acac)L^1: 0.01 mmol.

TABLE 3 Epoxidation of cyclooctene under various conditions[a] catalysed by VO(acac)L^{1-4}

Entry	Complex	Solvent	Substrate/oxidant	Oxidant	Time (min)	Conversion (%)
1	VO(acac)L^1	$CHCl_3$	1:3	TBHP	140	89
2	VO(acac)L^1	$CHCl_3$	1:3	H_2O_2	140	2
3	VO(acac)L^1	$CHCl_3$	1:3	$NaIO_4$	140	12
4	VO(acac)L^2	$CHCl_3$	1:3	TBHP	140	81
5	VO(acac)L^2	$CHCl_3$	1:3	H_2O_2	140	2
6	VO(acac)L^2	$CHCl_3$	1:3	$NaIO_4$	140	8
7	VO(acac)L^3	$CHCl_3$	1:3	TBHP	140	89
8	VO(acac)L^3	$CHCl_3$	1:3	H_2O_2	140	5
9	VO(acac)L^3	$CHCl_3$	1:3	$NaIO_4$	140	9
10	VO(acac)L^4	$CHCl_3$	1:3	TBHP	140	45
11	VO(acac)L^4	$CHCl_3$	1:3	H_2O_2	140	-
12	VO(acac)L^4	$CHCl_3$	1:3	$NaIO_4$	140	3

[a]Reaction conditions: $CHCl_3$ as solvent: 5 ml; cyclooctene: 0.5 mmol; TBHP: 1.5 mmol; catalyst: 0.01 mmol.

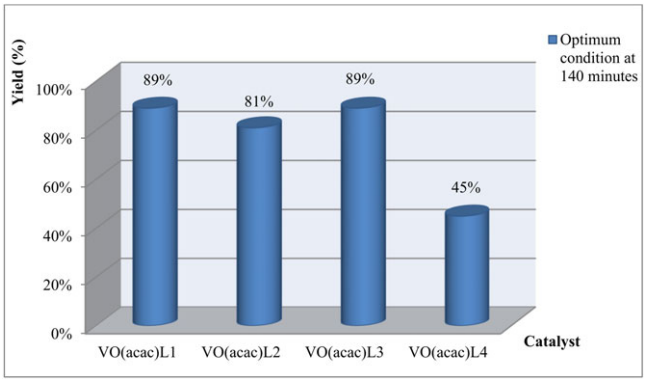
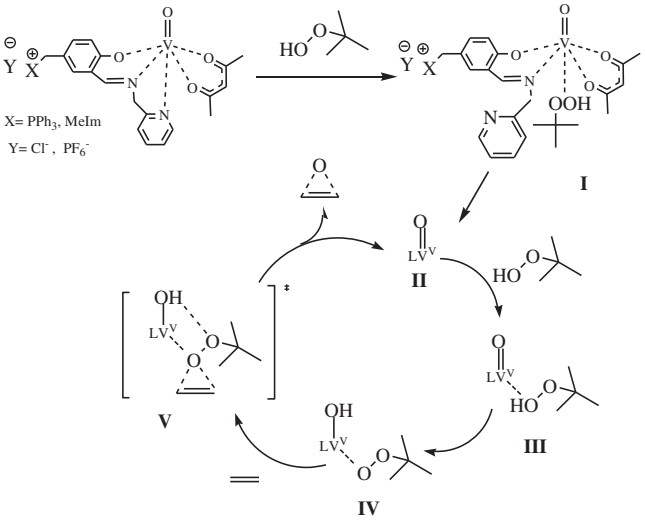


FIGURE 4 Yields of cyclooctene epoxide obtained under reflux conditions in the presence of VO(acac)L^{1-4} complexes. (Reaction conditions: $CHCl_3$ as solvent, 5 ml; cyclooctene, 0.5 mmol; TBHP, 1.5 mmol; catalyst, 0.01 mmol)



SCHEME 2 Proposed mechanism for the epoxidation of cyclooctene catalysed by oxovanadium complexes VO(acac)L^{1-4} in the presence of TBHP

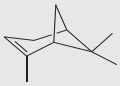
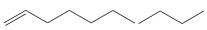
by PF_6^- to give VO(acac)L^3, and keeping the cation (triphenylphosphonium), the catalytic activity of the complex was not changed appreciably, whereas this trend was not seen in the case of methylimidazolium cation in which the catalytic activity of VO(acac)L^2, containing Cl^- counter anion, is higher than that of VO(acac)L^4 with PF_6^- counter anion. Thus the effect of the ionic part of these task-specific ionic liquid vanadyl Schiff base complexes in epoxidation of cyclooctene depends on the nature of cation and anion of the ionic part.

The mechanistic aspects of the catalytic epoxidation of alkenes by V(IV) complexes were reviewed by Conte *et al.*[25] Polar and radical mechanisms were proposed. Therefore, we propose the mechanism sketched in Scheme 2. We suggest that the nitrogen of pyridine in pendant group of Schiff base ligand is coordinated at the opposite site of V=O bond in a weak linkage and firstly it can be substituted by TBHP in catalytic reaction (Scheme 2). Thus in similar to five-coordinated V(IV) Schiff base complexes,[26–28] after coordination of TBHP to the vanadyl centre, it oxidizes to LV^V=O moiety. As we discussed above concerning the solvent effect, the change in the dielectric constant and/or polarity of the solvent can have an effect on the catalytic activity of the catalyst. Based on our search we did not find any reports of the ionic character of V(IV) Schiff base complexes in epoxidation reaction being investigated. Thus, here, we study this by choosing the groups on the ligands to give them ionic character, in order to investigate the effect of the ionic nature of the complexes (catalysts) on their catalytic activity. It seems that the catalytic activity of a complex varies by changing in its ionic character. These observations are in agreement with polar mechanism

(Scheme 2). Changing the ionic character of the catalyst changes the interaction of the catalyst with its surrounding. As this ionic change can impose a large change in polarity of the catalyst, the catalytic activity can be highly affected. By changing the cationic moiety from triphenyphosphonium in L^1 to imidazolinium in L^2, the catalytic activity is decreased (Figure 4). It can be suggested that positive charge on phosphonium can be distributed on the three phenyl groups and thus would have a small effect on the interaction of the catalyst with its surrounding (substrate and TBHP) resulting in favourable interaction with substrate and oxidant in the transition state (**V** in Scheme 2), whereas, in the case of imidazolinium, the positive charge is concentrated on this moiety and has a greater effect on the interaction of the catalyst with reaction media and retards the formation of activated complex **V**. This is in agreement with the observation that changing the counter anion of imidazolinium moiety from Cl^- in VO(acac)L^2 to PF_6^- in VO(acac)L^4 leads to a marked decrease in catalytic activity. It is clear that there is a need for very deep experimental and theoretical study to confirm these observations, which is beyond the scope of this research.

Furthermore, the epoxidation of various alkenes catalysed by VO(acac)L^1 was investigated under optimized conditions. The obtained results are presented in Table 4. As seen from this table, cyclic alkenes were more efficiently converted to their corresponding epoxides than linear alkenes.

TABLE 4 Epoxidation of alkenes catalysed by VO(acac)L^1 in presence of TBHP under reflux conditions[a]

Alkene	Time (min)	Conversion (%)
	140	89
	300	57
	240	18
	240	13
	300	2

[a]Reaction conditions: $CHCl_3$ (5 ml), alkene (0.5 mmol), TBHP (1.5 mmol), catalyst (0.01 mmol).

3.7.2 | Oxidation of methylphenyl sulfide

It is known that vanadium-dependent haloperoxidases[29,30] and model complexes catalyse the oxidation of sulfides (thioethers) to sulfoxides and sulfones.[31,32] We also investigated the catalytic activity of Schiff base complexes VO(acac)$L^{1–4}$ in mimicking sulfoxidation using methylphenyl sulfide as a model substrate. The reaction conditions were optimized for the maximum oxidation of methylphenyl sulfide by studying three different parameters (oxidation media, catalyst amount and reaction time) under solvent-free conditions. The results for VO(acac)L^1 catalyst are summarized in Table 5 and for VO(acac)$L^{2–4}$ catalysts in Table 6. The blank reactions were carried out under the optimum conditions using 4 mmol of MeSPh and 4.4 mmol of TBHP without any catalyst with solvent-free conditions, but no appreciable conversions were seen. In all other cases, i.e. increasing the reaction time,

TABLE 5 Oxidation of methylphenyl sulfide under various conditions[a] catalysed by VO(acac)L^1

Run	Substrate/oxidant	Oxidant	Catalyst amount (mmol)	Time (min)	Conversion (%)	Sulfoxide (%)	Sulfone (%)
1	1:1.1	TBHP	0.024	2	85	100	—
2	1:1.1	TBHP	0.024	10	100	—	100
3	1:1.2	TBHP	0.024	2	95	9	91
4	1:1.5	TBHP	0.024	2	100	—	100
5	1:1.1	TBHP	0.012	2	89	51	49
6	1:1.1	TBHP	0.048	2	100	—	100
7	1:1.1	H_2O_2	0.024	2	10	100	—
8	1:1.1	H_2O_2	0.024	10	18	67	33
9	1:1.5	H_2O_2	0.024	2	13	81	19
10	1:3	H_2O_2	0.024	2	29	42	58
11	1:1.1	TBHP	—	5	No reaction	—	—
12	1:1.1	H_2O_2	—	5	No reaction	—	—

[a]Reaction conditions: solvent free; substrate (methylphenyl sulfide): 4 mmol. Optimum conditions with high conversion: substrate/oxidant (TBHP) ratio of 1:1.1 led to 85% yield for conversion of MePhS (sulfide) to MePhSO (sulfoxide) in 2 min with 0.024 mmol of VO(acac)L^1 catalyst (entry 1).

TABLE 6 Oxidation of methylphenyl sulfide under various conditions[a] catalysed by VO(acac)L^{2-4}

Run	Complex	Substrate/oxidant	Oxidant	Catalyst amount (mmol)	Time (min)	Conversion (%)	Sulfoxide (%)	Sulfone (%)
1	VO(acac)L^2	1:1.1	TBHP	0.024	2	85	100	—
2	VO(acac)L^2	1:1.1	H_2O_2	0.024	2	9	100	—
3	VO(acac)L^2	1:1.1	TBHP	0.012	2	50	91	9
4	VO(acac)L^2	1:1.1	TBHP	0.048	2	100	—	100
5	VO(acac)L^2	1:1.5	TBHP	0.024	2	100	—	100
6	VO(acac)L^3	1:1.1	TBHP	0.024	4	82	100	—
7	VO(acac)L^3	1:1.1	H_2O_2	0.024	4	5	100	—
8	VO(acac)L^3	1:1.1	TBHP	0.012	4	18	67	33
9	VO(acac)L^3	1:1.5	TBHP	0.048	4	92	—	100
10	VO(acac)L^4	1:1.1	TBHP	0.024	10	76	100	—
11	VO(acac)L^4	1:1.1	H_2O_2	0.024	10	5	43	57
12	VO(acac)L^4	1:1.1	TBHP	0.012	10	42	59	41
13	VO(acac)L^4	1:1.1	TBHP	0.048	10	100	—	100
14	VO(acac)L^4	1:1.5	TBHP	0.024	10	100	—	100
15	VO(acac)L^{2-4}	1:1.1	TBHP	—	10	No reaction	—	—

[a]Reaction conditions: solvent free; substrate (methylphenyl sulfide): 4 mmol. Optimum conditions with high conversion: substrate/oxidant (TBHP) ratio of 1:1.1 with 0.024 mmol of VO(acac)L^{2-4} catalyst (entries 1, 6, 10).

increasing the substrate/oxidant ratio and increasing the catalyst concentration, the selectivity to sulfoxide was decreased and the reaction proceeded towards sulfone production. Thus the catalytic reactions of the VO(acac)L^{1-4} catalysts were carried out under optimized conditions: substrate/oxidant ratio of 1:1.1, catalyst amount of 0.024 mmol and time of 2 min for VO(acac)$L^{1,2}$, 4 min for VO(acac)L^3 and 10 min for VO(acac)L^4. The results are presented in Figure 5. According to these results, the order of activity is VO(acac)L^1 ~ VO(acac)L^2 > VO(acac)L^3 > VO(acac)L^4 with yields 85, 82 and 76%, respectively. It is seen that

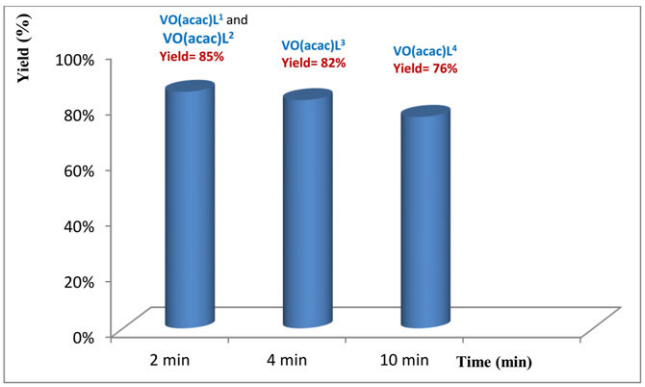


FIGURE 5 Yields of methylphenyl sulfoxide obtained under optimized conditions in the presence of VO(acac)L^{1-4} complexes. (Substrate/oxidant ratio, 1:1.1; catalyst amount, 0.024 mmol; reaction time, 2 min for VO(acac)$L^{1,2}$, 4 min for VO(acac)L^3 and 10 min for VO(acac)L^4)

the catalytic activity of these complexes in the oxidation of methylphenyl sulfide was also affected by changing the ionic part of them. By changing the cation from phosphonium (in VO(acac)L^1) to imidazolinium (in VO(acac)L^2) with constant counter anion of Cl^-, the catalytic activity was not changed, but by changing the counter anion from Cl^- in VO(acac)$L^{1,2}$ to PF_6^- in VO(acac)$L^{3,4}$ the catalytic activity of the latter (VO(acac)$L^{3,4}$) was decreased where in the case of imidazolinium chloride (VO(acac)L^4) it was dramatic. Therefore, the good yield of products obtained when using complexes VO(acac)L^{1-3} can be related to the good mixing of them with other reactants in contrast to the poorly soluble complex VO(acac)L^4 in solvent-free condition and also to the high solubility of them in water and most organic solvents. Thus for these task-specific ionic liquid vanadyl Schiff base complexes, changing the counter anion has a greater effect than changing the cationic part on the catalytic activity in methylphenyl sulfide oxidation reaction, because of the effects on polarity and solubility of the complexes.

4 | CONCLUSIONS

In summary, task-specific ionic liquid Schiff base complexes of V(IV), VO(acac)L^{1-4}, have been synthesized and characterized. Spectroscopic studies showed a six-coordinated V(IV) structure in the solid state. Complexes

$VO(acac)L^{1-3}$ are quite soluble in water and also in other organic solvents. We investigated the effect of the ionic nature of these task-specific ionic liquid Schiff base complexes in epoxidation of cyclooctene and oxidation of methylphenyl sulfide under optimized conditions. It was found that the catalytic activity of these complexes was affected by their ionic nature in epoxidation of cyclooctene and oxidation of methylphenyl sulfide, with the nature of the counter anion having a greater effect on the catalytic activity than the cationic moiety.

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