

Article

Ionic Liquids Based on Oxidoperoxido-Molybdenum(VI) Complexes with a Chelating Picolinate Ligand for Catalytic Epoxidation

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Abstract: Ionic oxidoperoxido-molybdenum(VI) complexes of the type [Cat][MoO(O₂)₂(pic)], with pic = N,O-chelated picolinate ligand and Cat = monocation, were prepared in high yields (82–95%) from the precursor complex [H₃O][MoO(O₂)₂(pic)] via [H]⁺ cation exchange for 1-ethyl-3-methylimidazolium [EMIM]⁺, 1-butyl-3-methylimidazolium [BMIM]⁺, 1-octyl-3-methylimidazolium [OMIM]⁺, *N*-cetylpyridinium [C₁₆Py]⁺, and *N*-methyl-*N,N,N*-triethylammonium [Aliquat]⁺. The structure and purity of the ionic compounds were assessed by ¹H and ¹³C NMR, FT-IR, and elemental analysis (C, H, N), and the electrochemical properties were studied by differential pulse voltammetry (DPV) and cyclic voltammetry (CV). The [Cat][MoO(O₂)₂(pic)] compounds showed promising catalytic epoxidation activity based on the model reaction of *cis*-cyclooctene with *tert*-butyl hydroperoxide as oxidant. The type of cation influenced the physical state of the compound and the catalytic performance.

Keywords: ionic liquid complexes; oxidoperoxidomolybdenum; picolinate; catalysis; epoxidation

1. Introduction

Oxidodiperoxido-metal complexes of the type [MO(O₂)₂(L)_{*n*}] with M=Mo, W and L an organic Lewis base (*n* = 1, 2), were discovered by Mimoun et al. [1] in 1969 and reported as stable complexes. These types of complexes were found to be effective oxidation catalysts with a broad substrate scope, such as olefins [2–8], alkyl benzenes [9,10], amines [11–13], alcohols [8,13–15], sulphides [13,16–24], and chalcogenides [25].

Neutral Mimoun type mononuclear complexes are well established catalysts for olefin epoxidation, as highlighted in several reviews [6,7,26–29]. These catalytic systems may use eco-friendly oxidants such as hydrogen peroxide [3,4,30–38] and *tert*-butyl hydroperoxide (TBHP) [8,30,35,39–45], and different types of solvents: catalyst/H₂O₂ systems with organic solvents [3,4,30–34], water [35], ionic liquids [36,37,46] or without solvent [38]; and catalyst/TBHP systems with an organic solvent [8,30,39–41,47–51], water [35], or without solvent [42–45].

As opposed to neutral Mimoun type mononuclear complexes, their ionic versions with the general formula [Cat]_{*m*}[MoO(O₂)₂(L)_{*n*}] (Cat = cation, *m* = 1, 2) have hardly been studied in the field of catalysis. In 1987, Dengel et al. [52] reported that the dianionic complex [PPh₄]₂[MoO(O₂)₂(L)], with L = oxalate, was inactive as a catalyst for alkene epoxidation. In the 90's, the monoanionic

complexes $[\text{Bu}_4\text{N}][\text{MoO}(\text{O}_2)_2(\text{L})]$, $[\text{CTA}][\text{MoO}(\text{O}_2)_2(\text{L})]$ (CTA = cetyltrimethylammonium) and $[\text{H}_3\text{O}][\text{MoO}(\text{O}_2)_2(\text{L})]$, with L = picolate *N*-oxido, were reported as sources of oxygen (not as catalysts, i.e., the metal complexes were used in approximately stoichiometric amounts relative to the substrate) for oxidizing different glycols, alcohols, olefins, sulphides, sulfoxides and amines [53–59]. Later, in 2005, Maiti et al. [13] reported the anionic complex $[\text{PPh}_4][\text{MoO}(\text{O}_2)_2(\text{QO})]$, with QOH = 8-quinolinol, as an active catalyst for the oxidation of alcohols, sulphides and amines using H_2O_2 as oxidant. However, in the same decade, Garah et al. [31,32,34,60] found that several monoanionic complexes of the type $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{L})_n]$ ($[\text{Cat}]^+$ = tetraorganophosphonium type cation, and L = conjugated base of 2-hydroxybenzoic acid, benzoic acid [31], pyridine-2-carboxylic acid [32], or an oxime such as (hydroxyphenyl)ethenone [60], salicylaloxime [34] and pyridine-2-carboxaloxime [32]) were inactive as catalysts for olefin epoxidation using H_2O_2 as oxidant (co-additives were required for olefin epoxidation to occur).

More recently, Zare et al. [43,44] reported the first active olefin epoxidation catalyst of the type $[\text{Cat}]_m[\text{MoO}(\text{O}_2)_2(\text{L})_n]$ with L = phox = 2-(2'-hydroxyphenyl)-5,6-dihydro-1,3-oxazine ($[\text{Cat}]^+$ was not specified). In these studies, TBHP was used as oxidant, as opposed to the previous catalytic epoxidation studies using the ionic complexes with H_2O_2 as oxidant.

In this work, ionic complexes of the type $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{L})]$ were synthesized, characterized, and tested as epoxidation catalysts with TBHP, without the need of additional co-catalysts or co-additives. A set of compounds was prepared possessing L = 2-picolate (pic) and $[\text{Cat}]^+$ = *N*-cetylpyridinium $[\text{C}_{16}\text{Py}]^+$, *N*-methyl-*N,N,N*-trioctylammonium $[\text{Aliquat}]^+$, 1-octyl-3-methylimidazolium $[\text{OMIM}]^+$, 1-butyl-3-methylimidazolium $[\text{BMIM}]^+$ or 1-ethyl-3-methylimidazolium $[\text{EMIM}]^+$. These compounds and their synthetic precursor $[\text{H}_3\text{O}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ were tested as catalysts in the model epoxidation reaction of *cis*-cyclooctene/TBHP, at 70 °C, giving up to quantitative epoxide yield at 3 h reaction.

2. Materials and Methods

Commercially available reagents were used for the syntheses of the complexes and catalytic tests. The anion exchange resin Amberlite IRA-400-OH (hydroxide ion-exchange capacity = 1.4 meq. mL^{-1}) was purchased from Supelco. The synthetic precursor $[\text{H}_3\text{O}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ (pale yellow solid) was prepared by adapting a known procedure [61]. With the exception of ethanol used in the syntheses (96%, Valente & Ribeiro, Belas, Portugal), which was distilled before use, all other chemicals were used as received from commercial suppliers: molybdenum(VI) oxide (99.5%, Alfa Aesar, Kandel, Germany), hydrogen peroxide (30% *w/v*, Panreac), $[\text{EMIM}][\text{Br}]$, $[\text{OMIM}][\text{Br}]$ and $[\text{BMIM}][\text{Cl}]$ (all >98%, Solchemar), *N*-cetylpyridinium chloride (>98%, BDH), Aliquat 336 (>97%, Sigma-Aldrich, Algés, Portugal), *cis*-cyclooctene (95% Alfa Aesar, Kandel, Germany), 2-*trans*-octene (97%, Sigma-Aldrich, Algés, Portugal), cyclododecene (96%, mixture *cis/trans*, Aldrich, Algés, Portugal), *tert*-butyl hydroperoxide (5.5 M in decane, Aldrich, Algés, Portugal), 30% aqueous hydrogen peroxide (Riedel-de-Haën), anhydrous α,α,α -trifluorotoluene ($\geq 99\%$, Sigma-Aldrich, Algés, Portugal), acetonitrile (gradient grade, Honeywell), 1,2-dichloroethane (99%, Aldrich, Algés, Portugal), and undecane ($\geq 99\%$, Aldrich, Algés, Portugal) as the internal standard.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX400 spectrometer at room temperature unless specified otherwise. Chemical shifts are reported downfield in parts per million (ppm). Melting points were determined using a Stuart Scientific apparatus. The IR spectra were measured on a Perkin Elmer 683 and are reported as either in NaCl, pellets or neat. The elemental analyses were performed on a CHNS Series Thermo Finnigan-CE Instruments Flash EA 1112, under standard conditions (combustion reactor at 900 °C, GC column furnace at 65 °C, multiseparation SS GC column, He flow of 130 mL/min, and O_2 flow of 250 mL min^{-1}). Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were used for electrochemical analyses. Electrochemical cells and glass were pre-washed with a mixture of sulphuric acid and 30% hydrogen peroxide (1:1). All the material was then washed with Mili-Q water and ethanol, oven-dried at 80 °C, and then cooled to room temperature and stored in a desiccator prior to use. HPLC grade acetonitrile was dried over calcium hydride, distilled, and kept

under an argon atmosphere. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP), which was pre-dried and stored in a desiccator. Each sample was vacuum-dried, and dissolved in 0.1 M TBAP in MeCN directly in the electrochemical cell, in order to obtain a 1 mM solution of the analyte. The solutions were deoxygenated under argon flow. A potentiostat/galvanostat Autolab model 12 (Echo-Chemie) was used coupled to a computer with GPES 4.9 software. The electrochemical cell was made of quartz and contained the following electrodes: (a) working electrode of platinum, internal diameter 1.6 mm (BIAS Inc, MF-2000); (b) auxiliary electrode of platinum wire, and (c) standard calomel reference electrode (SCE) in 3 M KCl. CV experiments were performed in the potential range -1.2 to $+2.0$ V and DPV in the range -1.5 to 2.0 V with a modulation time of 0.05 s, scan rate of 50 mV/s, interval time of 0.5 s, step potential of 0.006 V, modulation amplitude of 0.06 V, and the voltammograms were recorded after 5 cycles.

[H₃O][MoO(O₂)₂(pic)] (1). Molybdenum trioxide (1.5 g, 10.4 mmol) was dissolved in 30% hydrogen peroxide (15 mL) at 40 to 45 °C overnight. The solution obtained was cooled to 0 °C. A solution of picolinic acid (1.28 g, 10.4 mmol) in water (2 mL) was then added slowly. The reaction mixture was left overnight in the fridge to form a light yellow precipitate. This solid was separated by filtration and vacuum-dried to provide [H₃O][MoO(O₂)₂(pic)] as a yellow powder (2.6 g, 80%). Spectral data were as described in refs [27,62]—FT-IR (cm⁻¹) $\tilde{\nu} = 3480$ (vs, broad), [OH]; 1685 (s), [(C=O)_{as}]; 973 (s), [Mo=O]; 850(s), [O–O]; 572 (s), [(MoO₂)_{as}] and 542 (m), [(MoO₂)_{sym}].

[EMIM][MoO(O₂)₂(pic)] (2). [EMIM][Br] (0.136 g, 0.71 mmol) was dissolved in distilled water (10 mL) and passed through an anion exchange column loaded with Amberlite IRA-400(OH) (2.6 mL; 5 eq., flux rate 8 BV h⁻¹). The resultant [EMIM][OH] solution was slowly added to a 0.1 M aqueous solution (10 mL) of **1** (1 mmol; 1.4 eq.). The reaction mixture was stirred at room temperature for 1 h, and subsequently extracted several times using dichloromethane. The combined extracts were subjected to solvent evaporation followed by vacuum-drying at room temperature, giving the pure product as a yellow powder (0.28 g, 96%). m.p. 82 – 86 °C. ¹H NMR (400.13 MHz, CDCl₃): δ (ppm) = 9.10 (s, 1H); 8.16 (d, 1H, J = 4.4 Hz); 8.03 (d, 1H, J = 7.5 Hz); 7.84 (t, 1H, J = 7.5 Hz); 7.38–7.31 (m, 3H); 4.34 (q, 2H, J = 7.3 Hz); 4.02 (s, 3H); 1.57 (t, 3H; J = 7.3 Hz). ¹³C NMR (100.63 MHz, CDCl₃): δ (ppm) = 169.51; 147.51; 145.29; 139.16; 136.69; 127.40; 124.52; 123.81; 121.92; 45.58; 36.66; 15.49. Selected FT-IR (cm⁻¹) $\tilde{\nu} = 3144$ (m), 3107(m), 3067(s), 1684(vs), 1600(s), 1572(s), 1474(m), 1444(m), 1426(m), 1375, 1324(vs), 1291(s), 1257(m), 1173(s), 1149(s), 1045(m), 944(vs), 870(s), 857(vs), 772, 758(s), 711(s), 696(s), 648(m), 633(m), 581(m), 530(m), 446(m). Elemental analysis calcd. (%) for C₁₂H₁₅MoN₃O₇: C 35.22; H 3.69; N 10.27; found: C 35.50; H 3.57; N 9.91.

[BMIM][MoO(O₂)₂(pic)] (3). [BMIM][Cl] (0.25 g, 1.43 mmol) was dissolved in distilled water (20 mL) and passed through an anion exchange column loaded with Amberlite IRA-400(OH) (5.2 mL; 5 eq., flux rate 8 BV h⁻¹). The resultant [BMIM][OH] solution was slowly added to a 0.1 M aqueous solution (20 mL) of **1** (2 mmol; 1.4 eq.). The reaction mixture was stirred at room temperature for 1 h and then extracted several times using dichloromethane. The combined extracts were subjected to solvent evaporation followed by vacuum-drying at room temperature, giving the pure product as a yellow viscous liquid (0.51 g, 82%). m.p. 44 – 52 °C. ¹H NMR (400.13 MHz, CDCl₃): δ (ppm) = 9.17 (s, 1H); 8.16 (d, 1H; J = 3.6 Hz); 8.02 (d, 1H; J = 7.6 Hz); 7.84 (t, 1H, J = 7.2 Hz); 7.38–7.33 (m, 3H); 4.26 (t, 2H, J = 7.2 Hz); 4.02 (s, 3H), 1.87 (t, 2H, J = 7.2 Hz); 1.36 (q, 2H, J = 7.2 Hz); 0.93 (t, 3H, J = 7.2 Hz). ¹³C NMR (101.63 MHz, CDCl₃): 169.52; 147.54; 145.30; 139.12; 137.11; 127.37; 124.50; 123.74; 122.13; 50.12; 36.66; 32.19; 19.61; 13.56. Selected FT-IR (cm⁻¹) $\tilde{\nu} = 3437$ (vs), 3166 (m), 3123(m), 2956, 2934, 2872, 1678(vs), 1651(s), 1601(s), 1577(m), 1469(m), 1442(m), 1382, 1334(s), 1286(m), 1257, 1238, 1159, 1111, 1158(m), 1091, 1042, 951(s), 873(m), 863(s), 833(m), 823, 757(m), 711, 694, 650, 622, 583, 525, 443. Elemental analysis calcd. (%) for C₁₄H₁₉MoN₃O₇: C 38.46; H 4.38; N 9.61; found: C 38.52; H 4.17; N 9.34.

[OMIM][MoO(O₂)₂(pic)] (4). [OMIM][Br] (0.165 g, 0.71 mmol) was dissolved in distilled water (10 mL) and passed through an anion exchange column loaded with Amberlite IRA-400(OH) (2.6 mL; 5 eq., flux rate 8 BV h⁻¹). The resultant [OMIM][OH] solution was slowly added to a 0.1 M aqueous

solution (10 mL) of **1** (1 mmol; 1.4 eq.). The reaction mixture was stirred at room temperature for 1 h and then extracted several times using dichloromethane. The combined extracts were subjected to solvent evaporation followed by vacuum-drying at room temperature, giving the pure product as an amorphous solid (0.32 g, 91%). m.p. 106–108 °C. ^1H NMR (400.13 MHz, CDCl_3): δ (ppm) = 9.17 (s, 1H); 8.19 (d, 1H; J = 4.8 Hz); 8.03 (d, 1H, J = 7.4 Hz); 7.83 (t, 1H, J = 7.4 Hz); 7.37–7.21 (m, 3H); 4.27 (t, 2H, J = 6.8 Hz); 4.05 (s, 3H); 1.90 (t, 2H, J = 6.8 Hz); 1.62 (s, 2H); 1.32–25 (m, 8H); 0.86 (t, 3H, J = 6.4 Hz). ^{13}C NMR (101.63 MHz, CDCl_3): δ (ppm) = 169.47; 147.54; 145.27; 139.09; 136.83; 127.33; 124.48; 123.82; 122.18; 50.42; 36.65; 31.80; 30.29; 29.12; 29.03; 26.37; 22.70; 14.19. Selected FT-IR (cm^{-1}) $\tilde{\nu}$ = 3561, 3146(m), 3108(m), 2926(m), 2855(m), 1681(s), 1602(m), 1572(m), 1469(m), 1328(m), 1290(m), 1257, 1240, 1159(m), 1092, 1045(m), 1023(m), 946(s), 860(s), 762(m), 735(m), 711(m), 696(m), 651(m), 623(m), 583(m), 530, 482. Elemental analysis calcd. (%) for $\text{C}_{18}\text{H}_{27}\text{MoN}_3\text{O}_7$: C 43.82; H 5.52; N 8.52; found: C 44.02; H 5.48; N 8.47.

$[\text{C}_{16}\text{Py}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ (**5**). $[\text{C}_{16}\text{Py}][\text{Cl}]$ (0.240 g, 0.71 mmol) was dissolved in distilled water (10 mL) and passed through an anion exchange column loaded with Amberlite IRA-400(OH) (2.5 mL; 5 eq., flux rate 8 BV h^{-1}). The resultant *N*-cetylpyridinium hydroxide solution was slowly added to a 0.1 M aqueous solution (10 mL) of **1** (1 mmol; 1.4 eq.). The reaction mixture was stirred at room temperature for 1 h. The product was filtered using a Hirsh funnel, washed with distilled water, and vacuum-dried at room temperature to give the pure product as a pale-yellow powder (0.39 g, 91%). m.p. 89–92 °C. ^1H NMR (400.13 MHz, CDCl_3): δ (ppm) = 8.97 (d, 2H, J = 4.0 Hz); 8.46–8.44 (m, 1H); 8.16–8.02 (m, 4H); 7.83 (bs, 1H); 7.36 (bs, 1H); 4.75 (bs, 2H); 2.04 (bs, 2H); 1.62 (bs, 2H); 1.33–1.23 (m, 24H); 0.88 (bs, 3H). ^{13}C NMR (100.63 MHz, CDCl_3): δ (ppm) = 169.43; 147.54; 145.27; 144.76; 139.05; 128.72; 127.32; 124.47; 62.79; 32.06; 31.84; 31.06; 29.82; 29.66; 29.50; 29.15; 26.28, 22.82; 14.26. Selected FT-IR (cm^{-1}) $\tilde{\nu}$ = 3447(m), 3118(m), 3081(m), 3053(m), 2916(vs), 2850(s), 1684(vs), 1654, 1629(m), 1603(m), 1498(w), 1483(m), 1471(m), 1458(m), 1443, 1329(s), 1295(m), 1259(m), 1152(s), 1047(m), 947(vs), 861(vs), 781, 760, 712(m), 695(m), 649, 585. Elemental analysis calcd. (%) for $\text{C}_{27}\text{H}_{42}\text{MoN}_2\text{O}_7$: C 53.82; H 7.03; N 4.65; found: C 54.02; H 7.03; N 4.59.

$[\text{Aliquat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ (**6**). $[\text{Aliquat}][\text{Cl}]$ (0.285 g, 0.71 mmol) was dissolved in ethanol (10 mL) and passed through an anion exchange column loaded with Amberlite IRA-400(OH) (2.6 mL; 5 eq., flux rate 8 BV h^{-1}). The resultant $[\text{Aliquat}][\text{OH}]$ solution was slowly added to a 0.1 M aqueous solution (10 mL) of **1** (1 mmol; 1.4 eq.). The reaction mixture was stirred at room temperature for 1 h, and then subjected to solvent evaporation. The concentrated solution was diluted with distilled water and subsequently extracted several times using chloroform. The combined extracts were subjected to solvent evaporation followed by vacuum-drying at room temperature, giving the pure product as a yellow coloured, room temperature ionic liquid (RTIL) (0.45 g, 95%). ^1H NMR (400.13 MHz, CDCl_3): δ (ppm) = 8.20 (d, 1H, J = 4.4 Hz); 8.02 (d, 1H, J = 7.7 Hz); 7.80 (t, 1H, J = 7.7 Hz); 7.33 (m, 1H); 3.31 (t, 6H, J = 8.4 Hz); 3.18 (s, 3H); 1.60–1.45 (m, 6H); 1.35–1.25 (m, 30H), 0.87 (t, 9H, J = 6.8 Hz). ^{13}C NMR (101.63 MHz, CDCl_3): δ (ppm) = 169.38; 147.78; 145.29; 138.79; 127.11; 124.35; 61.98; 48.77; 31.99; 31.78; 29.56; 29.52; 29.40; 29.21; 29.16; 26.44; 22.79; 22.72; 22.53; 14.21. Selected FT-IR (cm^{-1}) $\tilde{\nu}$ = 2924(s), 2854(m), 1679(s), 1602(m), 1468(m), 1443, 1327(m), 1290, 1256, 1155, 1044, 947(s), 859(s), 761, 710(m), 696, 651(m), 583(m), 500(s). Elemental analysis calcd. (%) for $\text{C}_{31}\text{H}_{58}\text{MoN}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$: C 52.98; H 8.89; N 3.99; found: C 53.10; H 8.55; N 3.61.

Catalytic epoxidation tests: The catalytic tests were carried out at 70 °C under air in a closed borosilicate batch reactor with 5 mL capacity, equipped with a V-shaped magnetic stirring bar and a valve for sampling. Typically, the reactor was loaded with 1 mol.% molybdenum complex relative to the substrate: the substrate (1.8 mmol), the oxidant (2.74 mmol) and a solvent (1 mL). The solvents used were α,α,α -trifluorotoluene (TFT), acetonitrile and 1,2-dichloroethane (DCE). The loaded reactor was immersed in a thermostatically controlled oil bath heated at 70 °C, with a stirring rate of 1000 rpm; this was taken as the initial instant of the epoxidation reaction.

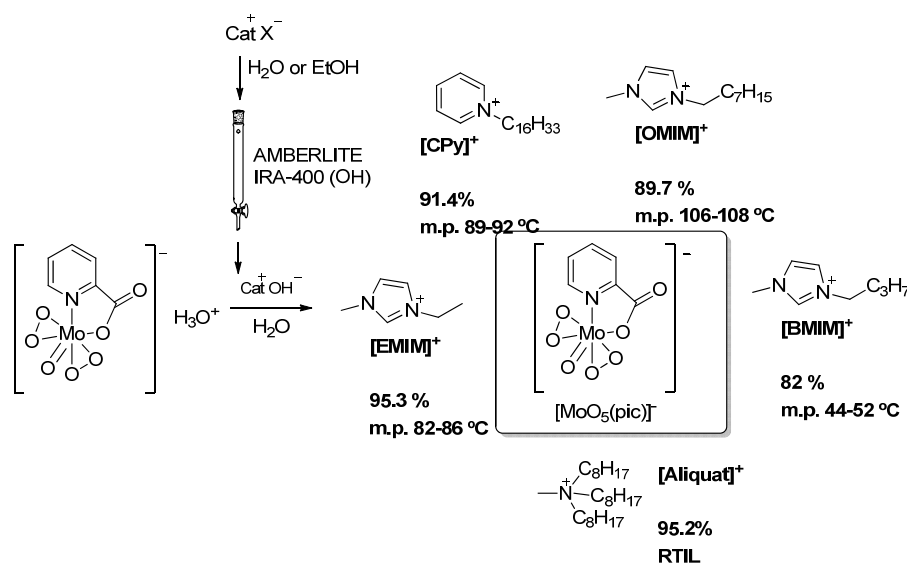
Prior to sampling and analysis of freshly prepared samples, the reactor was quenched in cold water, and the reaction mixture was subjected to centrifugation (3500 rpm). The catalytic

reactions were monitored using an Agilent 7820A GC equipped with a capillary column (HP-5 30 m × 0.320 mm × 0.25 mm), a flame ionization detector, and undecane was used as internal standard. Product identification was carried out using a GC-MS (Trace GC 2000 series (Thermo Quest CE instruments)-DSQ II mass detector (Thermo Scientific)) equipped with an Agilent J&W DB1 capillary column (DB-1 MS, 30 m × 0.25 mm × 0.25 mm), with He as carrier gas. TOF were based on catalytic results at 6 h reaction. Conversion was calculated using the formula $100 \times [((\text{initial molar concentration of Cy}) - (\text{molar concentration of Cy at time t})) / (\text{initial molar concentration of Cy})]$ and cyclooctene oxide (CyO) selectivity was calculated using the formula $100 \times [(\text{molar concentration of CyO at time t}) / ((\text{initial molar concentration of Cy}) - (\text{molar concentration of Cy at time t}))]$.

3. Results and Discussion

3.1. Characterization of the Ionic Complexes

Five ionic compounds of the type $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ with pic = picolate and $[\text{Cat}]^+$ = N-containing organic cation (pyridinium, imidazolium or ammonium), were prepared according to Scheme 1. Specifically, the precursor $[\text{H}_3\text{O}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ (**1**) was reacted with a hydroxide of the desired monocation ($[\text{Cat}]\text{OH}$, with $[\text{Cat}]^+$ = $[\text{EMIM}]^+$, $[\text{BMIM}]^+$, $[\text{OMIM}]^+$, $[\text{C}_{16}\text{Py}]^+$, $[\text{Aliquat}]^+$), giving the desired $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ (**2–6**) in good yields (82–95%). For these reactions, the base $[\text{Cat}]\text{OH}$ was prepared from the corresponding salt $[\text{Cat}]\text{X}$ using the anion exchange resin Amberlite IRA 400-OH. The physical state of the ionic complexes is dependent on the type of cation. It is observed a solid organic salt for $[\text{Cat}]^+$ = OMIM^+ (**4**) (m.p. 106–108 °C); ionic liquids (ILs) for $[\text{Cat}]^+$ = $[\text{EMIM}]^+$ (**2**), $[\text{BMIM}]^+$ (**3**), and $[\text{C}_{16}\text{Py}]^+$ (**5**) (the melting points of the complexes were 82–86 °C, 44–52 °C and 89–92 °C, respectively) and room temperature ionic liquid (RTIL) for $[\text{Cat}]^+$ = $[\text{Aliquat}]^+$ (**6**) [63].



Scheme 1. Synthesis route leading to the complexes $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$.

The chemical structures and purities of compounds **2–6** were checked by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and FT-IR spectroscopies, and elemental analysis (C, H, N). Experimental elemental analysis data is in good agreement with the calculated values. The characteristic IR bands of **1** and its $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ derivatives are very similar with respect to the carbonyl group ($\nu(\text{C}=\text{O})_{\text{as}} = 1685$ vs. $1678\text{--}1684$ cm^{-1}), but are slightly shifted with respect to the oxido and peroxido groups in the $\text{MoO}(\text{O}_2)_2$ moiety ($\nu(\text{Mo}=\text{O}) = 973$ vs. $944\text{--}950$ cm^{-1} ; $\nu(\text{O}=\text{O}) = 850$ vs. $854\text{--}862$ cm^{-1} ; $\nu(\text{Mo}(\text{O}_2)_2)_{\text{as}} = 572$ vs. $582\text{--}585$ cm^{-1} and $\nu(\text{Mo}(\text{O}_2)_2)_{\text{sym}} = 542$ vs. $525\text{--}550$ cm^{-1}) [27,62]. None of the compounds exhibited the characteristic band of the carbonyl group attributed to the free picolinic acid (2-pyridinecarboxylic

acid) at 1722 cm^{-1} [64]. All spectral data (IR, ^1H , and ^{13}C NMR), as well as elemental analysis (C, H, N), suggested pure compounds containing an anionic metal complex.

The electrochemical properties of the ionic complexes were studied by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) (Figure 1) using as reference SCE (standard calomel electrode in 3 M KCl). In general, the voltammograms in DPV showed one predominate oxidation peak at approximately 1.45 V, while the corresponding wave in CV is irreversible.

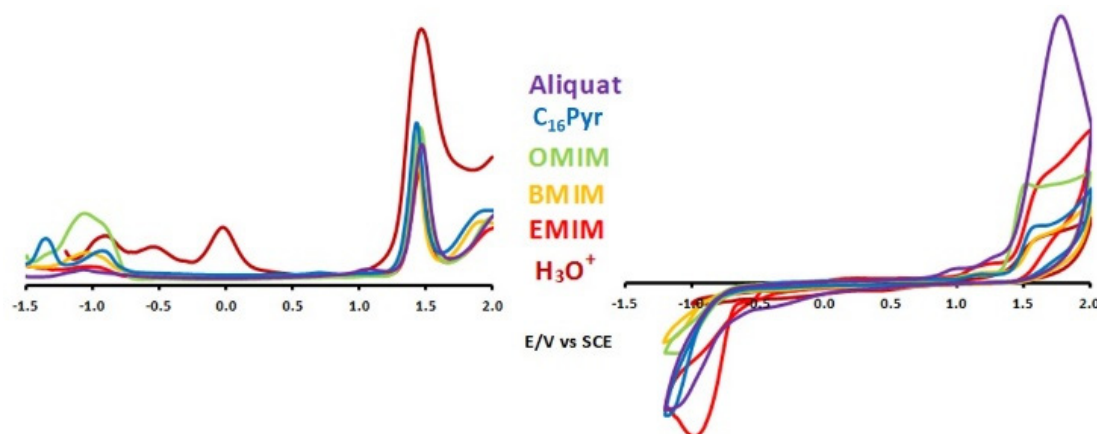


Figure 1. Voltammograms of the $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ compounds with $[\text{Cat}]^+ = [\text{H}_3\text{O}]^+$, $[\text{EMIM}]^+$, $[\text{BMIM}]^+$, $[\text{OMIM}]^+$, $[\text{C}_{16}\text{Py}]^+$ or $[\text{Aliquat}]^+$: on the left voltammograms by DPV; on the right voltammograms by CV.

The additional oxidation wave at ca. +2.0 V was detected for most complexes. In general, the complexes exhibited the Ep_2 reduction peak between -0.89 and -1.07 V. The compounds with $[\text{C}_{16}\text{Py}]^+$ and $[\text{H}_3\text{O}]^+$ cations exhibited one (-1.36 V) or two (-0.55 V and -0.02 V) additional reduction peaks, respectively (Table 1). Overall, the DPV and CV results suggested that the variation of the cation structure does not significantly affect the electrochemical profile of the anionic complex.

Table 1. Potential of oxidation and reduction (V) of the $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ compounds.

$[\text{Cat}]^+$	Ep_1	Ep_2	Ep_3	Ep_4	Ep_5	Ep_6
$[\text{Aliquat}]^+$		-1.07			$+1.47$	$+2.07$
$[\text{C}_{16}\text{Py}]^+$	-1.36	-0.93			$+1.43$	$+1.97$
$[\text{OMIM}]^+$		-1.05			$+1.45$	$+1.99$
$[\text{BMIM}]^+$		-1.04			$+1.43$	$+1.90$
$[\text{EMIM}]^+$					$+1.45$	$+1.98$
$[\text{H}_3\text{O}]^+$		-0.89	-0.55	-0.02	$+1.46$	n.d. ¹

¹ n.d. = not distinguishable.

3.2. *cis*-Cyclooctene Catalytic Epoxidation

The complexes $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ with $[\text{Cat}]^+ = N$ -containing organic cation, and the synthetic precursor with $[\text{Cat}]^+ = \text{H}_3\text{O}^+$, were studied as catalysts in the model epoxidation reaction of Cy with TBHP as oxidant, at $70\text{ }^\circ\text{C}$ (Figure 2 and Table 2). The TBHP: Cy molar ratio was 1.6, and $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ was added in an amount equivalent to 1 mol% of molybdenum relative to Cy. For all compounds already prepared, the turnover number (TON) was greater than unity ($13\text{--}100\text{ mol}_{\text{Cy}}\text{ mol}_{\text{Mo}}^{-1}$), and up to 100% Cy conversion was reached (Figure 2a). Without catalyst, conversion was negligible. Cyclooctene oxide (CyO) was the main product formed in up to 100% yield (Figure 2b). These results demonstrate the ability of the catalysts $[\text{Cat}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ to trigger the epoxidation process with TBHP and without requiring co-catalysts.

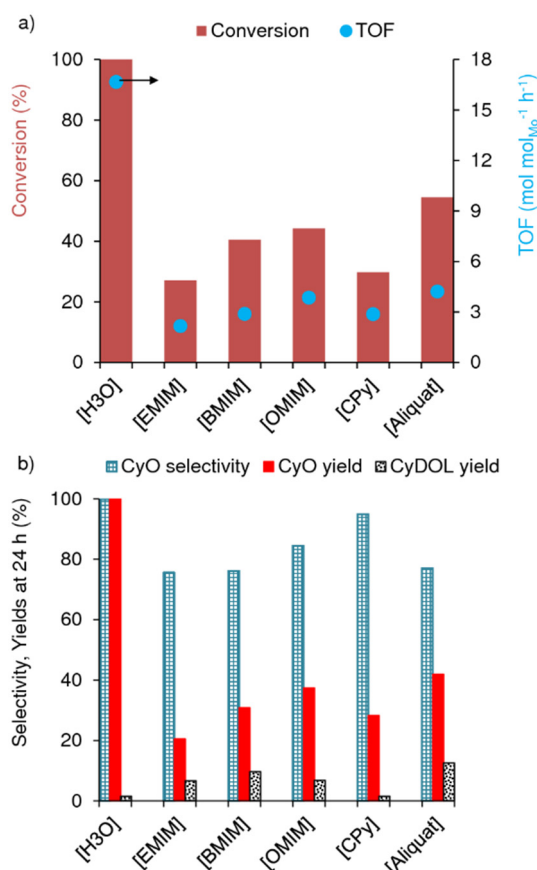


Figure 2. Catalytic epoxidation of Cy with TBHP, in the presence of [Cat][MoO(O₂)₂(pic)] (only [Cat] is indicated in the abscissa axis for the sake of simplicity): (a) conversion of Cy at 24 h, and turnover frequency (TOF); (b) CyO selectivity, and yields of the epoxide (CyO) and corresponding diol by-product (CyDOL), at 24 h. Reaction conditions: 1 mol.% Mo, molar ratio TBHP: Cy = 1.6, TFT as solvent, 70 °C.

Mechanistic studies for molybdenum-catalysed epoxidation of olefins with alkyl hydroperoxide oxidants corroborate a Lewis acid-base reaction in which the molybdenum compound acts as a Lewis acid and the alkyl hydroperoxide (TBHP) as a Lewis base, leading to an active oxidising species that is involved in the oxygen atom transfer to the olefin, finally giving the epoxide product [65–69]. In the present study, the catalytic epoxidation system [Cat][MoO(O₂)₂(pic)]/TBHP is an alternative strategy to that firstly reported by Herbert et al. [2] involving the use of [Bu₄N][MoO(O₂)₂(pic)] as stoichiometric oxidant (not as catalyst) and Co(acac)₂ as catalyst. Later, the same group reported olefin epoxidation using stoichiometric amounts of neutral complexes [MoO(O₂)₂(L)₂] (L = pyrazole or 3,5-dimethylpyrazole), with or without a hydroperoxide oxidant, and suggested that the epoxidation reaction mechanism could proceed via Sharpless [65] or Thiel type mechanisms [2,69–71]. In the present study, only 1 mol% complex was used, thus if the complex acted as oxidant (and considering one atom of active oxygen per peroxido ligand), it would lead to a maximum Cy conversion of 2%, which is negligible. The catalytic cycle of the system [Cat][MoO(O₂)₂(pic)]/TBHP likely involves a Lewis acid-base type mechanism with TBHP as the oxygen atom source.

The influence of the type of *N*-containing cation, i.e., imidazolium, pyridinium or ammonium derivatives, on the performance of [Cat][MoO(O₂)₂(pic)] type catalysts was studied, using TFT as solvent at 70 °C. The turnover frequency (TOF, mol_{Cy} mol_{Mo}⁻¹ h⁻¹) increased in the order 2 (2.1) < 3 (2.9) ≈ 5 (2.9) < 4 (3.9) ≈ 6 (4.2) (Figure 2a). The parent compound 1 exhibited the highest activity, leading to 100% CyO yield at 3 h, compared to 42% CyO yield at 24 h with 1,2-cyclooctanediol (CyDOL) as by-product (13% yield) for the best-performing catalyst possessing a *N*-containing cation,

namely **6** (Figure 2b). The catalyst **6** was tested using different types of solvents (TFT, DCE, MeCN), which indicated that the most favourable one was TFT. Specifically, Cy conversion at 24 h increased in the order MeCN (27%) < DCE (39%) < TFT (55%). The poorer results for MeCN as solvent may be partly due to its coordinating ability since, according to the above mechanistic considerations, coordinating solvents may compete with the oxidant molecules for coordination to the molybdenum centre.

To gain insights into the electronic features of the complexes, their electrochemical properties were studied (discussed above). No clear correlation could be established between catalytic activity and the electrochemical properties (Figure 3). The type of cation did not considerably affect the electrochemical properties of the anionic complex. Hence, other factors seem to influence the catalytic performance. Focusing on the set of compounds with *N*-containing cations, specifically those with imidazolium type cations, it seems that the activity increases with increasing carbon chain length of the alkyl substituent, being highest for [Cat]⁺ = [OMIM]⁺. The compound with [Aliquat]⁺, which possesses three C8 carbon chains, led to the highest Cy conversion at 24 h (55%). Possibly, for this set of compounds, longer carbon chains favoured the dissolution of the catalyst in the reaction medium, enhancing the overall reaction rate. On the other hand, the transition state formed via coordination of TBHP to the metal centre (to give an active oxidizing species) may be influenced by the presence of the hydronium cation in the best-performing catalyst [H₃O][MoO(O₂)₂(pic)] (**1**). For example, the mechanism may involve partial dissociation of the pic ligand and the hydronium cation may influence the protonation of an oxido ligand by TBHP. However, validation of this hypothesis would require more detailed studies, e.g., computational chemistry.

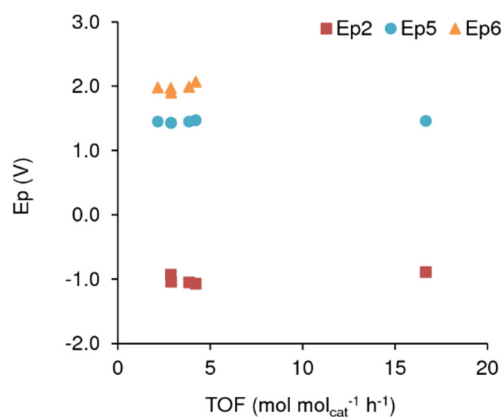


Figure 3. TOF versus CV results (Ep₂, Ep₅ and Ep₆). Reaction conditions: 1 mol.% Mo, molar ratio TBHP: Cy = 1.6, TFT as solvent, 70 °C.

Table 2 compares the results for the prepared catalysts to literature data for [MoO(O₂)₂(L)_n] type complexes tested as catalysts for the Cy/TBHP reaction [35,39,41–45,72–76]. The neutral complex [MoO(O₂)₂(2,2'-bipy)] led to 28% conversion at 24 h/70 °C, in water (entry 23) [35]. In the reaction temperature range 25–55 °C, relatively low Cy conversions were reached in the presence of the neutral complexes [MoO(O₂)₂(L)] with L = chiral oxazoline type ligand (38% conversion at 22 h/25 °C, in toluene) [73], L = ethyl[3-pyridin-2-yl]-1H-pyrazol-1-yl]acetate (22% conversion at 24 h/55 °C, in DCE) [42] or L = 2,2'-bipy (34% conversion at 6 h/55 °C, in TFT) [76] (entries 10, 19, 22). In the temperature range 55–75 °C, high Cy conversions in the range 90–100% were reached at 6–24 h for neutral complexes [MoO(O₂)₂(L)] with L = 2-(2-pyridyl)-benzimidazole [72], 2-[3(5)-pyrazolyl]pyridine [39,74], 2-(1-pentyl-3-pyrazolyl)pyridine [75] (using chlorinated organic solvents, entries 9, 18, 21), L = 4,4'-di-*tert*-butyl-2,2'-bipyridine [35] (using H₂O as solvent, entry 24), or L = bis(pyrazolyl)methane [45] (without solvent, entry 25). The anionic complex [MoO(O₂)₂(phox)][−] (the cation was not specified) led to 45% conversion at 20 min/80 °C (no solvent) [44].

Overall, it is not trivial to make clear comparisons of the results between different studies due to the different reaction conditions used. Nevertheless, a rough comparison to literature data for

complexes consisting of neutral or ionic $[\text{MoO}(\text{O}_2)_2(\text{L})_n]$ suggests that $[\text{H}_3\text{O}][\text{MoO}(\text{O}_2)_2(\text{pic})]$ possesses relatively good activity for Cy epoxidation with TBHP (82%/100% CyO yield at 1 h/3 h reaction, 70 °C).

Table 2. Comparison of the catalytic results of the compounds prepared to literature data for complexes consisting of neutral or ionic $[\text{MoO}(\text{O}_2)_2(\text{L})_n]$ tested for the model reaction of Cy/TBHP [35,39,41–45,72–76].

	Catal [a]	Ox:Cy [b]	Mo [b] (mol%)	Solvent	T (°C) [c]	t (h) [c]	Conversion (%) [d]	Selectivity (%) [e]	Ref
1	1	1.52	1	TFT	70	1/2/3	82/93/100	100/100/100	This work
2	2	1.52	1	TFT	70	6/24	13/27	94/76	This work
3	3	1.52	1	TFT	70	6/24	17/41	82/76	This work
4	4	1.52	1	TFT	70	6/24	23/44	77/85	This work
5	5	1.52	1	TFT	70	6/24	17/30	87/95	This work
6	6	1.52	1	TFT	70	6/24	25/55	84/77	This work
7	6	1.52	1	MeCN	70	6/24	5/27	100/76	This work
8	6	1.52	1	DCE	70	6/24	16/39	91/81	This work
9	$[\text{MoO}(\text{O}_2)_2(\text{pbim})]$	1.53	1	DCE	70	6/24	81/98	100	[72]
10	$[\text{MoO}(\text{O}_2)_2(\kappa^2\text{-N,O-L})_2]$	1.5	2.5	Toluene	25	22	15/38	100	[73]
11	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR1})]$	1.0	0.4	CHCl_3	65	1	TON [f]	100	[74]
12	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR2})]$	1.0	0.4	CHCl_3	65	1	TON [f]	100	[74]
13	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR3})]$	1.0	0.4	CHCl_3	65	1	TON [f]	100	[74]
14	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR4})]$	1.0	0.3	CHCl_3	65	1	TON [f]	100	[74]
15	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR5})]$	1.0	0.2	CHCl_3	65	1	TON [f]	100	[74]
16	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR6})]$	1.0	0.4	CHCl_3	65	1	TON [f]	100	[74]
17	$[\text{MoO}(\text{O}_2)_2(\text{pzpyR7})]$	1.0	0.2	CHCl_3	65	1	TON [f]	100	[74]
18	$[\text{MoO}(\text{O}_2)_2(\text{pzpy})]$	1.52	0.3	DCE	75	6	100	100	[39]
19	$[\text{MoO}(\text{O}_2)_2(\text{pypzEA})]$	1.52	0.1	DCE	55	24	22	100	[42]
20	$[\text{MoO}(\text{O}_2)_2(\text{bzpyppz})]$	1	0.5	CHCl_3	nm [g]	6	95	100	[41]
21	$[\text{MoO}(\text{O}_2)_2(\text{pent-pp})]$	1.52	0.9	DCE	55	6	90	100	[75]
22	$[\text{MoO}(\text{O}_2)_2(2,2'\text{-bipy})]$	1.5	1	TFT	55	6	34	100	[76]
23	$[\text{MoO}(\text{O}_2)_2(2,2'\text{-bipy})]$	1.53	1	H_2O	70	24	28	100	[35]
24	$[\text{MoO}(\text{O}_2)_2(\text{di-tBu-bipy})]$	1.53	1	H_2O	70	24	98	100	[35]
25	$[\text{MoO}(\text{O}_2)_2(\text{BPM})]$	1.53	1	-	55	6	100	100	[45]
26	$[\text{nm}][\text{MoO}(\text{O}_2)_2(\text{phox})]$ [g]	1	0.05	-	95	0.33	97	100	[43]
27	$[\text{nm}][\text{MoO}(\text{O}_2)_2(\text{phox})]$ [g]	1	0.05	-	80/85/95	0.33	45/69/99	100	[44]
28	$[\text{nm}][\text{MoO}(\text{O}_2)_2(\text{phox})]$ [g]	1	0.05	DCE	95	0.33	98	100	[44]

[a] pic = picolinate; pbim = 2-(2-pyridyl)-benzimidazole; ($\kappa^2\text{-N,O-L})_2$ = chiral oxazoline ligands; Pzpy = 2-[3(5)-pyrazolyl]pyridine, R1 = H, R2 = CH_3 , R3 = C_4H_9 , R4 = C_8H_{17} , R5 = C_8H_{37} , R6 = $\text{CH}_2\text{COOC}_2\text{H}_5$, R7 = $\text{CH}_2\text{CONHC}_{18}\text{H}_{37}$; pypzEA = ethyl[3-pyridin-2-yl]-1H-pyrazol-1-yl]acetate; bzpyppz = [2-(1-benzyl-1H-pyrazol-3-yl)pyridine]; pente-pp = 2-(1-pentyl-3-pyrazolyl)pyridine; 2,2'-bipy = 2,2'-bipyridine; di-tBu-bipy = 4,4'-di-tert-butyl-2,2'-bipyridine; BPM = bis(pyrazolyl)methane; phox = 2-(2'-hydroxyphenyl)-5,6-dihydro-1,3-oxazine. [b] Ox:Cy (Ox = TBHP) initial molar ratio and molybdenum mol% in relation to Cy. [c] Reaction temperature (T) and time (t). [d] Conversion of Cy. [e] Selectivity to CyO. [f] Conversions (calculated using the data reported in the experimental section and reported TOF at 65 °C (referred in the manuscript as TON, expressed as $\text{mol}_{\text{Cy}} \text{mol}_{\text{cat}}^{-1} \text{h}^{-1}$)) were in the range 45–61%. [g] nm = not mentioned.

Catalyst (1) was further explored using H_2O_2 as oxidant and acetonitrile as solvent (forming a single liquid phase), at 70 °C, which led to slower Cy reaction kinetics, without affecting epoxide selectivity (100% CyO selectivity): conversion at 1 h/3 h/6 h was 18%/30%/47%, compared to 82%/100% conversion at 1 h/3 h using TBHP as oxidant (the initial molar ratio Mo:Ox:oxidant was the same for the two oxidising systems). Possibly, the type of active species may be different for the two oxidants [68,70,71,77] and/or the presence of coordination solvents (water added together with H_2O_2 and acetonitrile) may lead to competition with the reactants in the coordination to the molybdenum centre. A similar trend was reported previously for Mo-catalysed epoxidation systems [78].

The catalytic system of 1/TBHP was tested with different substrates (cyclododecene and trans-2-octene), at 70 °C (Table 3). The corresponding epoxides were the main reaction products. The substrate reactivity decreased in the order Cy > trans-2-octene > cyclododecene. The higher reactivity of Cy compared to cyclododecene may be partly associated with steric effects (higher steric hindrance for the latter). Nevertheless, a comparative study for the cyclic versus linear C8 substrates suggests that other factors may also be important, such as electronic ones. A higher energy density of the C=C double bond may favour the attack of the nucleophilic olefin on an electrophilic oxidising species [79], to give the epoxide product.

Table 3. Olefin epoxidation with TBHP, in the presence of **1** ^[a].

Substrate	Time (h)	Conv. ^[b] (%)	Select. ^[c] (%)
cis-Cyclooctene	1/2/3	82/93/100	100/100/100
trans-2-Octene	1/3/4	35/78/84	100/97/95
Cyclododecene	1/3/4	33/65/71	97/95/95

^[a] Reaction conditions: initial molar ratio Mo:Olefin:oxidant = 1:100:152, 1 mL of cosolvent, 70 °C. ^[b] Olefin conversion. ^[c] Epoxide product selectivity. Byproducts included the respective diols.

The higher reactivity of Cy than cyclododecene may be related with important steric effects in the reaction of the bulkier olefin, as observed in a previous work of some of us [80]. The epoxide selectivity was excellent (100%) in the case of Cy and very high for the remaining olefins (95–97%) Table 3.

4. Conclusions

Compounds of the general formula [Cat][MoO(O₂)₂(L)] with L = picolinate and [Cat]⁺ = [EMIM]⁺, [BMIM]⁺, [OMIM]⁺, [C₁₆Py]⁺ and [Aliquat]⁺, were prepared in high yields. The CV and DPV analysis indicated that variation of the cation structure does not significantly affect the electrochemical properties of the complex anion. This is the only catalytic study which follows the studies by Garah et al. [31,32,34,60] for [Cat]_m[MoO(O₂)₂(L)_n] type complexes as epoxidation catalysts using TBHP as oxidant. The type of cation may influence the catalytic performance. The complex with [Cat]⁺ = [H₃O]⁺ (**1**) was the most effective catalyst with Cy as substrate and TBHP as oxidant, leading to 100% epoxide yield at 3 h reaction, 70 °C. Catalyst (**1**) was also active for the epoxidation of (linear) trans-2-octene and (bulkier) cyclododecene. A comparative study for H₂O₂ or TBHP as oxidant, indicated that the latter was more favorable, enhancing the reaction kinetics. This catalyst is one of the most active complexes consisting of neutral or ionic [MoO(O₂)₂(L)_n] reported so far. The cation exchange for an N-containing cation, i.e., imidazolium, pyridinium, or ammonium derivatives, does not necessarily lead to an improvement in catalytic performance, which highlights the favourable simplicity of (**1**).

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