V(IV), Fe(II), Ni(II) and Cu(II) complexes bearing 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate: application as catalysts for the cyclooctane oxidation

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V(IV), Fe(II), Ni(II) and Cu(II) complexes bearing 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate: application as catalysts for the cyclooctane oxidation

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Abstract

Water-soluble compounds $[VOCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ (pz = pyrazol-1-yl) **1**, $[FeCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **2**, $[NiCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **3** and $[Cu\{CH_3SO_2OCH_2C(pz)_3\}_2](OTf)_2$ **4** were obtained by reactions between the corresponding metal salts and 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate, $CH_3SO_2OCH_2C(pz)_3$. They were isolated as air-stable solids and fully characterized by IR, FTIR, NMR (for **2**), EPR (for **1**), ESI-MS(+/-), elemental analysis and (for **4**) single-crystal X-ray diffraction. In all, half- (**1**–**3**) or full-sandwich (**4**), compounds the C-scorpionate ligand shows the *N*,*N*,*N*-coordination mode.

3 and **4** appear to provide the first examples of a Ni(II) and a full-sandwich Cu(II) compound respectively, bearing that scorpionate ligand. Compound **3** is the first Ni(II) tris(pyrazol-1yl)methane type complex to be applied as catalyst for the oxidation of alkanes.

Compounds **1–4** exhibit catalytic activity for the peroxidative (with aq. H_2O_2) oxidation, in water/acetonitrile medium and under mild homogeneous conditions, of cyclooctane to the corresponding alcohol and ketone (yields up to *ca.* 27%). The effect of the presence of additives, such as nitric acid or pyridine, was studied.

Keywords: C-scorpionate, oxidation, catalysis, alkane, vanadium, iron, copper, nickel.

Introduction

Hydrotris(pyrazol-1-yl)-borates or –methanes and their derivatives, usually known as B- or C-homoscorpionates, respectively, have become well-established as ligands in coordination chemistry, and their complexes have made important contributions in different areas, namely in catalysis.[1] These compounds coordinate to transition metals and main group elements with the possibility of steric and electronic tuning by changing the 3- and/or 5-substituents of the pyrazolyl rings[1c-1f,2] and/or by functionalization of the central B or C atom. For example, replacement of the methinic proton by other functional groups can change the solubility characteristics of the ligands and their metal complexes, including the possibility of obtaining water-soluble complexes.[3] In this work, our attention was focused on the methanesulfonate tris(pyrazol-1-yl)methane ligand with a high hydrophilic nature, $CH_3SO_2OCH_2C(pz)_3$ (pz = pyrazol-1-yl), aiming to extend the still rather limited number of known complexes with this scorpionate ligand. The first examples are $[CrCl_3\{CH_3SO_2OCH_2C(pz)_3\}]$,[4] $[CoCl_2(H_2O)\{CH_3SO_2OCH_2C(pz)_3\}]$ [3d] and $[CuCl_2\{CH_3SO_2OCH_2C(pz)_3\}]_2$.[2d]

Homogeneous catalytic oxidation reactions generally involve the use of soluble salts or transition metal complexes in combination with oxidants like O_2, H_2O_2 or ROOH (R = alkyl). The industrial process for oxidation of cyclohexane uses dioxygen as O-donor in the presence, *e.g.*, of cobalt salts, at temperatures above 150 °C with conversion of *ca.* 4% for a selectivity of 85%.[5] Oxidation of saturated hydrocarbons using V(IV), Fe(II) and Cu(II) based C-scorpionate catalysts with hydrogen peroxide as oxidant was reported to give high conversion and selectivity.[1g,1h,2c,3c,6] Recently, Ni(II) complexes bearing bis(pyrazolyl)pyridine or tripodal 4N ligands were found[7a,b] to catalyse cyclohexane oxidation, although providing low yields of the oxygenated products and requiring stronger oxidants such as *meta*-chloroperbenzoic acid (*m*-CPBA).

Cyclooctane (and other cycloalkanes) oxidation to the corresponding cycloalcohol and cycloketone has been catalysed by polymer or silica-supported iron *N,N*–dimethyl-*N,N*-bis (pyridine-2-ylmethyl)-ethane-1,2-diamine (BPMEN) using dilute aqueous H_2O_2 as oxidant[7c] or copper coordination polymer capped polyoxometalate using *tert*-butyl hydroperoxide as an oxidant, under mild reaction conditions.[7d] In addition the iridium complexes of chelating triazoles and mesoionic carbenes act as catalysts for the oxidation of cyclooctane, under moderate conditions, to cyclooctanol and cyclooctanone.[7e]

Supported metalloporphyrines and metallophthalocyanines, *e.g.* anchored on functionalized aminoalkyl silica gel, polystyrene or montmorillonite K10, or encapsulated in zeolite NaX supercages as catalyst for cyclooctane oxidation.[8] Mesoporous chromium-silicate materials showed high activity and selectivity for the oxidation of cyclooctane to cyclooctanone, using dilute aqueous H_2O_2 or *tert*-butyl hydroperoxide as an oxidant, under mild reaction conditions.[9] Gold(III or I) complexes[10] and Keggin-type polyoxotungstates[11] catalyse the oxidation of cyclooctane (to the corresponding hydroperoxide, ketone and alcohol) by H_2O_2 in acetonitrile, at 60–80 °C. In addition, pyrazole Re complexes anchored in 3-aminopropyl functionalized silica gel[12a] or carbamated silica gel supported bis(maltolato)oxovanadium(IV or V) complexes[12b] act as catalysts for the oxidation of cyclooctane by molecular oxygen, under moderate conditions, to cyclooctanol and cyclooctanone.

In pursuit of our on-going work on the coordination chemistry of C-scorpionates and on the application of their complexes as catalysts for the partial oxidation of alkanes[1g,1h,6,13] we have now (i) studied the coordination behaviour of the scarcely used 2,2,2-

tris(pyrazol-1-yl)ethyl methanesulfonate, towards V(III), Fe(II), Ni(II) and Cu(II) centres; (ii) prepared the first examples of half-sandwich Ni(II) and full-sandwich Cu(II) complexes bearing the above ligand; and (iii) investigated the catalytic ability of the derived V(IV), Fe(II), Ni(II) and Cu(II) complexes for the peroxidative (with aqueous H_2O_2) oxidation of cyclooctane under mild conditions.

Experimental

General materials and procedures

VCl_3, $FeCl_2$, $NiCl_2$, $Cu(OSO_2CF_3)_2$, pyrazole, sulphur trioxide-trimethylamine complex, pyridine, nitric acid, hydrogen peroxide (50% aqueous solution), cyclooctane, nitromethane, diphenylamine (Aldrich), acetonitrile, tetrahydrofurane, diethyl ether, chloroform, methanol (Lab-Scan) were used as received from the supplier. $CH_3SO_2OCH_2C(pz)_3$ was obtained according to published methods.[2d,4]

Infrared spectra (4000-400cm^{-1}) were recorded on a BIO-RAD FTS3000MX in KBr pellets; wavenumbers are in cm^{-1}; abbreviations: *vs*, very strong; *s*, strong; m, medium; w, weak. Far infrared spectra FIR (400-200 cm^{-1}) were recorded on a Vertex 70 spectrophotometer in CsI pellets.

ESI$^+$/ESI$^-$ mass spectra were obtained on a VARIAN 500-MS LC ion trap mass spectrometer (solvent: MeOH; flow: 20 μL/min; needle spray voltage: ± 5 kV, capillarity voltage: ± 100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature (N_2): 350 ºC). For the MS spectra description, M denotes the complex part of compounds **1**–**4**.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance II+ 300 and 400 MHz (UltraShield^{TM} Magnet) at ambient temperature. δ values are in ppm relative to Me_4Si

(^{1}H and ^{13}C). EPR spectra were recorded on Bruker ESP 300E X-band spectrophotometer equipped with an ER 4111 VT variable-temperature unit.

UV-visible spectroscopic measurements were carried out on a PerkinElmer Lambda 750 UV-Visible spectrophotometer.

The C, H, N and S elemental analyses were carried out by the Micro analytical Service of the Instituto Superior Técnico.

The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to personal computer through a GPIB interface. Cyclic voltammograms (CV) were obtained in 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe, at a platinum disc working electrode (*d* = 1 mm). Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capil1ary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolyses. Ferrocene was used as an internal standard for the measurement of the oxidation potentials of the complexes; the redox potential values are quoted relative to the SCE by using as internal reference the ferrocene/ferricinium ($[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$) couple ($E_{1/2}^{ox}$ = 0.42 V *vs.* SCE in NCMe).[14]

Chromatographic measurements were carried out in a 'HP 5890 – Serie-II'; fused silica capillary column Hewlett-Packard; the stationary phase was polyethylene glycol: INNOWAX with parameters 25 m × 0.2 mm × 0.4 μm; carrier gas was helium with column pressure of 15 psi.

Synthesis and characterization of complexes

[$VOCl_2\{CH_3SO_2OCH_2C(pz)_3\}$] (**1**). A mixture of $CH_3SO_2OCH_2C(pz)_3$ (254 mg, 0.78 mmol) with VCl_3 (122 mg, 0.78 mmol) in methanol (20 mL) was stirred for *ca.* 24 h at 20–25°C, resulting in a green solution. The solution was filtered and concentred in *vacuo* to *ca.* one half, followed by slow addition of Et_2O (*ca.* 5 mL), resulting in the precipitation of a green solid of **1**. The latter was filtered off, washed with Et_2O (two portions of 10 mL) and dried in *vacuo* (0.17 g, 51.4% yield). **1** is soluble in H_2O ($S_{25°C} \approx$ 2.4 mg/mL), acetone and NCMe. IR (KBr pellet, cm^{-1}): 1522 and 1422 [s,ν(N=C), ν(N=N)], 1184 and 647 [s, ν(S=O), ν(C–S)], 976 [s, *ν*(V=O)]. Far–IR (CsI pellet, cm^{-1}): 346 and 388 [m, ν(V–Cl)]. EPR (DMSO, r.t.): a = 101.3 G, g = 1.9879. ESI^+: m/z 424 ($[M–Cl]^+$), 358 ($[M–Cl–pz]^+$). ε_{218} (H_2O) = 1.57×10^{-4} $L.mol^{-1}.cm^{-1}$. Anal. Calc. for $C_{12}H_{14}Cl_2N_6O_4SV$: (*mw* 460.2): C, 31.3; H, 3.1; N, 18.2; S, 7.0%. Found: C, 31.5; H, 3.5; N, 18.3; S, 7.3%.

[$FeCl_2\{CH_3SO_2OCH_2C(pz)_3\}$] (**2**). A solution of $CH_3SO_2OCH_2C(pz)_3$ (254 mg, 0.78 mmol) in methanol (10 mL) was added to a methanolic solution (15 mL) of $FeCl_2$ (100 mg, 0.79 mmol) at 20–25°C. The reaction mixture was stirred for *ca.* 24 h, resulting in a red solution. Concentration *in vacuo* of the filtered red solution followed by slow addition of Et_2O (*ca.* 5 mL) resulted in the precipitation of **2** as a red solid. This was filtered off, washed with Et_2O (two portions of 10 mL) and dried in *vacuo* (0.16 g, 46.0% yield). **2** is soluble in H_2O ($S_{25°C} \approx$ 2.0 mg/mL), MeOH and NCMe. IR (KBr pellet, cm^{-1}): 1522 and 1477 [s,ν(N=C), ν(N=N)], 1027 and 653 [s, ν(S=O), ν(C–S)]. Far–IR (CsI pellet, cm^{-1}): 308 and 228 [m, ν(Fe–Cl)]. ^1H NMR (MeOD-d_6): δ 7.66 [s, br, 3H, H3, $CH_3SO_2OCH_2C(pz)_3$], 7.35 [s, br, 3H, H5, $CH_3SO_2OCH_2C(pz)_3$], 6.40 [s, br, 3H, H4, $CH_3SO_2OCH_2C(pz)_3$], 5.63 [s, br, 2H, CH_2, $CH_3SO_2OCH_2C(pz)_3$], 3.34 [s, br, 3H, Me, $CH_3SO_2OCH_2C(pz)_3$]. $^{13}C\{^1H\}$ NMR (MeOD-d_6): δ 141.92 [s, C(3) and C(5) $CH_3SO_2OCH_2C(pz)_3$], 130.69 [s, C(4), $CH_3SO_2OCH_2C(pz)_3$], 106.92 [s, $CH_3SO_2OCH_2C(pz)_3$], 70.57 [s, $CH_3SO_2OCH_2C(pz)_3$], 37.12 [s, $CH_3SO_2OCH_2C(pz)_3$]. ^1H NMR (CD_3CN-d_6): δ 7.71 [s, br, 3H, H3, $CH_3SO_2OCH_2C(pz)_3$], 7.38 [s, br, 3H, H5, $CH_3SO_2OCH_2C(pz)_3$], 6.41 [s, br, 3H, H4, $CH_3SO_2OCH_2C(pz)_3$], 5.69 [s, br, 2H, CH_2, $CH_3SO_2OCH_2C(pz)_3$], 3.36 [s, br, 3H, Me, $CH_3SO_2OCH_2C(pz)_3$]. ESI$^+$: m/z 414 ([M–Cl]$^+$), 347 ([M–Cl–pz]$^+$). ε_{200} (H_2O) = 8.57×10^{-4} L.mol^{-1}.cm^{-1}. Anal. Calc. for $C_{12}H_{14}Cl_2FeN_6O_3S$ (*mw* 449.1): C, 32.1; H, 3.1; N, 18.7; S, 7.1%. Found: C, 32.6; H, 3.6; N, 19.3; S, 7.3%.

[$NiCl_2\{CH_3SO_2OCH_2C(pz)_3\}$] (**3**). A mixture of $CH_3SO_2OCH_2C(pz)_3$ (248 mg, 0.77 mmol) with a methanolic solution (50 mL) of $NiCl_2$ (100 mg, 0.77 mmol) was stirred for *ca.* 24 h at 20–25°C, forming a yellow solution. The resulting yellow solution was concentred in *vacuo* to *ca*. one half, followed by slow addition of Et_2O (*ca*. 5 mL) to yield a yellow solid of **3** which was filtered off, washed with Et_2O (two portions of 10 mL) and dried in *vacuo* (0.11 g, 33.0% yield). **3** is soluble in H_2O ($S_{25°C} \approx 2.0$ mg/mL) and NCMe. IR (KBr pellet, cm^{-1}): 1522 and 1417 [s,ν(N=C), ν(N=N)], 1033 and 641 [s, ν(S=O), ν(C–S)]. Far–IR (CsI pellet, cm^{-1}): 298 and 265 [m, ν(Ni–Cl)]. ESI$^+$: m/z 349 ([M–Cl–pz]$^+$), 282 ([M–Cl–2pz]$^+$). ε_{219} (H_2O) = 1.60×10^{-4} L.mol^{-1}.cm^{-1}. Anal. Calc. for $C_{12}H_{14}Cl_2N_6NiO_3S$ (*mw* 451.9): C, 31.9; H, 3.1; N, 18.6; S, 7.1%. Found: C, 31.7; H, 3.3; N, 18.9; S, 6.8%.

[$Cu\{CH_3SO_2OCH_2C(pz)_3\}_2$]($OTf)_2$ (**4**). A mixture of $CH_3SO_2OCH_2C(pz)_3$ (236 mg, 0.73 mmol) and $Cu(OTf)_2$ (132 mg, 0.37 mmol) in THF (20 mL) was stirred for *ca.* 24 h at 20–25°C yielding a blue solution. The latter was concentrated in *vacuo*, followed by slow addition of Et_2O (5 mL), resulting in the precipitation of solid **4**, which were separated by filtration and dried in air (0.147 g, 40.0% yield). The blue solid **4** was crystallized in Et_2O to give blue crystals. **4** is soluble in H_2O ($S_{25°C} \approx 2.2$ mg/mL) and CH_3CN. IR (KBr pellet, cm^{-1}): 1524 and 1413 [s,ν(N=C), ν(N=N)], 1054 and 640 [s, ν(S=O), ν(C–S)]. EPR (solid, 90 K): $a = 74.3$ G, $g = 2.1278$. ESI^+: m/z 707 ($[M–H^+]^+$), 354 ($[M]^{2+}$). ε_{219} (H_2O) = 3.43×10^{-4} $L.mol^{-1}.cm^{-1}$. Anal. Calc. for $C_{26}H_{26}CuF_6N_{12}S_4O_{12}$ (*mw* 1004.4): C, 31.1; H, 2.6; N, 16.7; S, 12.8%. Found: C, 31.1; H, 2.6; N, 16.4; S, 12.6%.

Crystal structure determination

The X-ray diffraction data were collected using a Bruker AXS-KAPPA APEX II with graphite monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[15a] on all the observed reflections. Absorption corrections were applied using SADABS.[15a] Structure was solved by direct methods by using the SIR-97 package[15b] and refined with SHELXL-2014/7.[15c] Calculations were performed using the WinGX System-Version 1.80.03.[15d] The hydrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2Ueq of the parent carbon atoms for phenyl and methylene residues and 1.5Ueq of the parent carbon atoms for the methyl groups. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed. The structure contained disordered non coordinated trifluoromethanesulfonate anion which was refined with the use of PART instruction. The occupancy of its two fragments refined to a ratio of 44.2 % and 55.8 %. CCDC

1412828 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic study

The catalytic oxidation reactions of complexes **1–4** were carried out in MeCN solvent (total volume is 10.0 mL) in thermostated Pyrex round bottom vessels and in open atmosphere, at 60 ºC. The catalyst (**1–4**) was used and introduced into the reaction mixture in the form of a stock solution in acetonitrile prepared by dissolving it in acetonitrile. Cyclooctane and promoter (if any) were then added in this order and the reaction started with the addition of hydrogen peroxide in a portion. (CAUTION: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). Initial concentrations of cyclooctane, catalyst, H_2O_2 and promoter (if used) were 0.25, 10^{-3}, 1 and 0.072 M, respectively. Solution samples were analysed by GC after addition of nitromethane (as a standard compound) using a method previously used by Shul'pin.[16] This method allows the estimate of concentrations of formed alkyl hydroperoxide, alcohol and ketone. Attribution of peaks was made by comparison with chromatograms of authentic samples. For precise determination of the product concentrations only data obtained after the reduction of the reaction sample with PPh_3 were typically used, taking into account that the original reaction mixture contained the three products: cycloalkxyl hydroperoxide (as the primary product), ketone and alcohol. When used, the oxygen radical trap, Ph_2NH, was applied in a stoichiometric amount relative to the oxidant.

Results and discussion

Synthesis and characterization of complexes

Compounds $[VOCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ (pz = pyrazol-1-yl) **1**, $[FeCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **2**, $[NiCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **3** and $[Cu\{CH_3SO_2OCH_2C(pz)_3\}_2](OTf)_2$ **4** were obtained from the reactions of VCl_3, $FeCl_2$, $NiCl_2$ and $Cu(OTf)_2$ (OTf = trifluoromethanesulfonate), respectively, with $CH_3SO_2OCH_2C(pz)_3$ (Scheme 1).

Scheme 1

The structures of the compounds were authenticated taking into account the microanalytical results, IR and far-IR spectroscopic data, ESI–MS as well as EPR (for **1**), NMR (for **2**) and single crystal X-ray diffraction (for **4**). In our compounds the scorpionate ligands act as *N,N,N*-tridentate chelators, disregarding a *N,N*-bidentate coordination mode previously found for $[CuCl_2\{CH_3SO_2OCH_2C(pz)_3\}]_2$[2d] or a *N,N,O*-tridentate binding type as found for the related $[Cu(Tpms^{Ph})(CyNC)]$ (Cy = cyclohexyl) ($Tpms^{Ph}$ = tris(3-phenylpyrazolyl)methane sulfonate].[2f]

The IR spectra of **1**–**4** exhibit ν(N=C) at *ca.* 1522 cm^{-1} and ν(N=N) in the range 1477 – 1413 cm^{-1} which are comparable to those obtained for other related scorpionate compounds.[1d-1f,2a,2b,6b-6f] The ν(S=O) or ν(C–S) vibrations of the methanesulfonate group are observed at the usual[2d,17] ranges of 1184 – 1027 and 653 – 640 cm^{-1}, respectively. The *v*(V=O) value at 976 cm^{-1} in **1** is comparable to those quoted for several oxivanadium(IV) complexes[2c,6b,6c] and also for those bearing the tris(1-pyrazolyl)borate ligand, such as $[VOCl\{HB(3,5Me_2pz)_3\}(Me_2Hpz)]$.[18]

The characterization by FIR was done for all complexes **1-4**.

The presence of the chloro ligands is confirmed by the occurrence, in their far-IR spectra, of two ν(M–Cl) bands at 388 and 346 (**1**), 308 and 228 (**2**), and 298 and 265 cm^{-1} (**3**) values comparable to those observed for other scorpionate chloro-copper complexes.[2d]

While the EPR spectrum of **1** shows the expected 8-line pattern of a paramagnetic V(IV) monomeric species (^{51}V, I = 7/2) with the typical values[19] of the *g* (1.9879) and *a* (101.3 G) parameters, that of **4** exhibits the usual pattern ^{63}Cu (I=3/2) also similar that of $[CuCl_2\{HC(pz)_3\}]$.[3c]

The N_5 coordination of Ni(II) is consistent with the ^1H NMR that shows its typical paramagnetic nature (Ni^{II}, S =1).[2c]

For complex **2**, **t**he equivalence of the pyrazolyl groups in solution is indicated by the unique broad resonances for each type of protons, *i.e.* for the 3, 4 or 5 position in the ring. Moreover, in the $^{13}C\{^1H\}$ NMR spectrum, the three carbon atoms from the pyrazolyl rings appear as singlets (141.92─130.69 ppm), and the carbon in apical position resonances at 106.92 ppm. The functional group $CH_3SO_2OCH_2$- is detected at 70.57 and 37.12 ppm.

The ESI^+ spectra of the compounds exhibit ion fragments at *m/z* corresponding to the loss of chloride ($[M–Cl]^+$ (in **1** and **2**) and loss of a chloride and a pyrazolyl group ($[M–Cl–pz]^+$ (in **1**–**3**). The molecular ion fragment could be observed only for the dicationic compound **4**.

All the complexes are stable in air and display high solubility in water (solubility *ca.* 2–2.4 $mg.mL^{-1}$), an important feature towards their application (see below) as catalyst precursors in aqueous media.

X-ray molecular structure

Compound **4** crystallizes in the triclinic space group *P-1* (Fig. 1a), the asymmetric unit includes half of the molecule where the metal is sitting in an inversion centre, and one disordered trifluoromethanesulfonate counter-ion. The copper atom is coordinated by six N-pyrazolyl atoms in a slightly distorted octahedral geometry (quadratic elongation of 1.024 and angle variance of 48.62 ^{o2}).[20]

The bond distances in the basal plane of the compound involve the N11, N11^{i}, N14 and the N14^{i} atoms and assume values of 1.999(3) and 2.021(4) Å (Fig. 1, legend) which are shorter than the apical bond involving N17 (and N17^{i}), 2.347(4) Å, as a consequence of Jahn-Teller effects. The minimum Cu···Cu distance equals the crystallographic *a* dimension (8.323 Å).

The conformations of the pyrazolyl rings differ in the molecule of **4**. Indeed, the Cu-N-N-C torsion angles assume values of 142.5, 169.0 and 170.9º. In an ideal case, such angles would be 180º and the metal atom would reside in the planes defined by the pyrazolyl rings. Such a fact may result from the presence of the -$CH_2OSO_2CH_3$ moiety which almost lies in the plane of one of the pyrazolyl rings, as confirmed by the value of the N16-C1-C2-O13 torsion angle of 168.3º, against 49.3º and -72.6º for N19-C1-C2-O13 and N13-C1-C2-O13, respectively.

Table 1. Crystallographic data for compound **4**.

	4
Empirical formula	$C_{26}H_{28}CuF_6N_{12}O_{12}S_4$
Formula weight	1006.38
Crystal system	triclinic

Space group	P -1
T (K)	150(2)
a (Å)	8.2321(7)
b (Å)	9.8695(8)
c (Å)	12.5776(10)
α (º)	101.763(3)
β (º)	103.543(2)
λ (º)	100.003(3)
V (Å^3)	945.92(14)
Z	1
Density (cal.) (Mg/m^3)	1.767
μ (mm^{-1})	0.905
F(000)	511
Rfl collected/unique/obs	10880 / 5584 / 3812
R_{int}	0.0320
R_1, wR_2 [$I > 2\sigma(I)$]	0.0679, 0.1943
R_1, wR_2 (all data)	0.1003, 0.2237
GOF on F^2	0.980

The crystal packing diagram in Fig. 1b shows the observed intermolecular π···π interactions which are also affected by the conformation of the rings. These interactions could stabilize the packing method and the coordination mode through the three pyrazolyl rings.

Figure 1

Electrochemical studies

In view of the potential application of the complexes **1**–**4** as catalyst precursors in oxidation processes (see below), their redox properties were studied by cyclic voltammetry (CV) (Table 2) and controlled potential electrolysis (CPE) in 0.2 M $[{}^{n}Bu_4N][BF_4]/NCMe$ solutions at a Pt (disc or gauze, respectively) electrode.

Complexes **1** and **2** exhibit single-electron irreversible cathodic waves at – 0.78 and – 0.38 V *vs.* SCE, respectively (Figure 2 for **1**) assigned to V(IV)/V(III) and to Fe(II)/Fe(I) reductions.

Complex **1** exhibits by CV a reversible monoelectronic (confirmed by CPE) anodic wave ($\mathbf{I}^{\mathbf{ox}}$) at 1.35 V *vs*. SCE, assigned to the V(IV) to V(V) oxidation. Complex **2** presents a reversible oxidation wave ($\mathbf{I}^{\mathbf{ox}}$) at 1.06 *vs.* SCE, conceivably due to the Fe(II)/Fe(III) oxidation.

For **3** and **4** no redox activity was found in the range from –2.00 to 2.00 V *vs*. SCE under the experimental conditions tested.

Table 2. Cyclic voltammetric data[a] for $[VOCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **1** and $[FeCl_2\{CH_3SO_2OCH_2C(pz)_3\}]$ **2**.

Complex	${}^{I}E_p^{ox}$ (${}^{I}E_{½}^{ox}$) ($\mathbf{I}^{\mathbf{ox}}$)	${}^{I}E_p^{red}$ ($\mathbf{I}^{\mathbf{red}}$)	Reference
1	(1.35)	–0.78	our work
2	(1.06)	–0.38	our work
$[CoCl_2(H_2O)\{CH_3SO_2OCH_2C(pz)_3\}]$[b]	1.10	–0.64	[3d]
$[CuCl_2\{CH_3SO_2OCH_2C(pz)_3\}]_2$[2d]	–	–0.70	our work

[a]Values in V ± 0.02 relative to SCE; scan rate of 200 mVs^{-1}, in NCMe.
[b]For comparative proposes.

Figure 2

Cyclooctane oxidation

Compounds **1–4** act as catalyst precursors for the oxidation of cyclooctane with 50% aqueous H_2O_2, at 60 ºC, in NCMe/H_2O. The main oxidation products of cyclooctane is a mixture of cylooctanol, cyclooctanone, and cyclooctyl hydroperoxide (Scheme 2). The quantification can be performed by gas chromatography and, using a method often applied[16] to ensure the precise quantification of the oxidation products present in the reaction solution, cyclooctyl hydroperoxide can be converted quantitatively to cyclohexanol by reduction with triphenylphosphine.

Scheme 2

The presence of cyclooctyl hydroperoxide was verified by additional GC injections of the samples before the treatment with triphenylphosphine.[16] This method allowed us to estimate the real concentrations of alkyl hydroperoxide, alcohol and ketone.

It is known that alkyl hydroperoxides, such as cyclooctyl hydroperoxide, are decomposed in the chromatograph to provide corresponding alcohols and ketones as main products. Nevertheless, the alkyl hydroperoxides decomposition also affords various byproducts obtained in the C-C bond cleavage process, which are trace detectable when compared to alcohol and ketone products.

Fig. 3 displays the effect of reaction time (until 32 h) on the overall (cyclooctanol + cyclooctanone) products yields without additive. Whereas for the V (**1**) and Cu (**4**) complexes the maximum yield is observed for *ca.* 8 h reaction time (followed by a decrease conceivably due to overoxidation), for the Fe (**2**) and Ni (**3**) compounds there is a continuous increase of the yield products with time, although not so marked, as at the first hours.

Table 3. Effect of the absence and presence of nitric acid and pyridine in the oxidation of cyclooctane catalysed by **1–4**[a]: total yield[b] (%) and ketone/alcohol molar ratio (in brackets)[c]

Entry		Additive	-				Nitric acid			Pyridine	
		Catalyst	**1**	**2**	**3**	**4**	**1**	**2**	**4**	**1**	**4**
1	Time (h)	1				4 (2:98)			5 (1:99)		
2		2	13 (32:68)	7 (6:94)	2 (2:98)	7 (2:98)	19 (61:39)	18 (59:41)	7 (2:98)	0.8 (0:100)	16 (38:62)
3		4	15 (34:66)	10 (7:93)	3 (2:98)	13 (4:96)	17 (73:27)	19 (71:29)	22 (2:98)	2 (0:100)	17 (60:40)
4		8	17 (38:62)	11 (9:91)	3 (3:97)	20 (8:92)	15 (80:20)	21 (73:27)	24 (5:95	4 (0:100)	16 (57:43)
5		10				21 (30:70)			25 (5:95)		
6		16				21 (30:70)			23 (6:94)		
7		20				20 (31:69)			24 (7:93)		
8		24	12 (51:49)	14 (11:89)	5 (5:95)	18 (34:66)	16 (83:17)	25 (79:21)	27 (12:88)	14 (1:99)	14 (51:49)
9		32	12 (56:44)	15 (12:88)	6 (6:94)	19 (39:61)	14 (84:16)	20 (82:18)	17 (14:86)	12 (23:77)	15 (53:47)

[a] Reaction conditions: cyclooctane (0.25 M), complex **1–4** (10^{-3} M), if used: {nitric acid or pyridine (0.072 M)} H_2O_2 (1.0 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b] Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh_3. [c] Cyclooctanone/cyclooctanol molar ratio.

Figure 3

The highest oxygenates yields in the first 20 h were provided by the Cu (**4**) (21%) and the V(**1**) (17%) compounds (Table 3, entries 5 and 4, respectively), but, after a prolonged time (30 h), the Fe (**2**) complex led to a 15% yield (Table 3, entry 9).

Interestingly, the full-sandwich of Cu complex **4** presents a high catalytic activity in spite of its coordinative saturation, thus acting as a sufficiently labile catalyst precursor.

In the following studies, the most active compounds **4**, **1** and **2** were used.

Effect of additives

The role of certain additives, in particular acids, on the catalytic oxidation of various cycloalkanes catalysed by Cu, Fe or V complexes is well known.[1g,1h,3c,6b-6f,13,21] Strong accelerating effects of pyridine and nitric acid was also described for Os-catalyzed oxidation of alkanes and other compounds.[22]

Hence, the influence of the presence of nitric acid (HNO_3) and pyridine (py) on the cyclooctanol and cyclooctanone yields was investigated.

Addition of HNO_3 had a promoting effect (Fig. 4a, Table 4) and enhanced total yields of 27% (**4**), 25% (**2**) and 19% (**1**) were obtained (Table 4). The favourable effect of acid presumably, as previously described for other systems,[1g,1h,3c,6b-6f,13,21] can be associated to ligand protonation leading to coordinative insaturation of the metal, and eventually to assist proton-transfer in the formation of hydroperoxyl ($HOO^•$) and hydroxyl ($HO^•$) radicals[1g,1h,22] involved in the proposed mechanism (see below).

Figure 4

In contrast, pyridine has usually an inhibiting effect although in the case of **4** the reaction is accelerated in the first 2 h (Fig.4b, Table 3).

The alcohol to ketone ratio (A/K) is known as an indicator for catalyst selectivity, reflecting the combined conversion of alkane either to directly the alcohol or to alkyl hydroperoxide, which subsequently is reduced to the alcohol as a result from the reduction with triphenylphosphine.[16] Thus, using the same nomenclature recently introduced by Haslinger *et al.*,[23] the A/K ratio is in fact a (alcohol+hydroperoxide)/ketone ratio (A+H)/K (Table S2). Comparison of alcohol/ketone ratio before and after the reduction with PPh_3, (Table S1) allow us to identify cyclooctyl hydroperoxide. For complex **4**, the (A+H)/K ratio along the reaction time was determined using conditions of Table 3. The ratio without reduction is drastically smaller compared to the values obtained after reduction with PPh_3. We can grossly estimate that the presence in the reaction mixture of cyclooctyl hydroperoxide is, under these conditions, around *ca.* 90% for the first hours of reaction time and *ca.* 50% after 24 hours reaction time, which means that alkyl hydroperoxide is the major oxidation product. Nevertheless, once the decomposition of cyclooctyl hydroperoxide upon injection is neither quantitative, nor well defined, the reduction with triphenylphosphine is, as mentioned before, necessary prior to GC injection for a precise quantitative analysis.[16]

The presence of pyridine promotes the selectivity towards the ketone. For instance, in the case of **4** and for 2 h reaction time, pyridine leads to the formation of a cyclooctanone:cyclooctanol ratio of 38:62 (entry 2, Table 3), whereas in the presence of nitric acid (entry 2, Table 3) or without any additive (entry 2, Table 3), that ratio is 2:98.

In fact, if we take into consideration that, although that the alkyl hydro peroxides decomposition in GC to the corresponding alcohol and ketones is accepted as *ca* 1:1 ratio, there are many factors (such as the injector type, temperature, substrates, etc.) that can substantially change this ratio, we can explain this ketone increase due to the presence of pyridine. In fact, is known the presence of such base induces the transformation of the hydroperoxide to ketone. A similar behaviour was reported for Os compounds.[22-24]

Effect of radical traps and mechanism

Cyclooctanol oxidation appears to involve a radical pathway with both C- and O-centred radicals, as observed for other C-scorpionate catalysed accloalkane oxidations.[1g,1h] In fact, the product yield decreases markedly when the reaction is carried out in the presence of either a C- or an O-centred radical trap (such as $CBrCl_3$ or Ph_2NH, respectively). Using **4**, at 8 h reaction time, the effect of Ph_2NH addition was more pronounced in the presence of HNO_3 (3.3 % yield, entry 2, Table 4), followed by the reaction in the absence of any promoter and by the reaction with the basic additive (entries 1-3, Table 4, to be compared with 20% yield in the absence of radical trap, entry 4, Table 3).

Table 4. Effect of the presence of Ph_2NH in the oxidation of cyclooctane catalysed by **4** in the absence and in the presence of an additive [a]: total yield[b] (%) and ketone/alcohol molar ratio (in brackets)[c]

Entry	Additive	Catalyst **4**
1	-	9.5 (15:85)
2	HNO_3	3.3 (6:94)
3	Py	10.6 (24:76)

[a]Reaction conditions: cyclooctane (0.25 M), complex **4** (10^{-3} M), Ph_2NH (1 M), additive if used (0.072 M), H_2O_2 (1 M) in acetonitrile at 60 °C after 8 h; total volume of reaction mixture is 10 mL. [b]Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh_3. [c]Cyclooctanone/cyclooctanol molar ratio.

The oxidation of cyclooctane (CyH) could proceed as follows (Scheme 3): metal-assisted decomposition of H_2O_2 could lead to the hydroxyl radical ($HO^\bullet$) which, upon H-abstraction from cyclooctane (CyH), would form the cyclooctyl radical ($Cy^\bullet$).[22] The formation of the $HO^\bullet$ radical should involve both M^n and M^{n-1} redox states (the former leading to H_2O_2 oxidation to $HOO^\bullet$ and the latter to the H_2O_2 reduction with liberation of $HO^\bullet$), as well as proton-transfer steps among H_2O_2, hydroperoxo and peroxo metal-species, similarly to what has been indicated[1g,1h,25] for some $V^{5+/4+}$, $Re^{7+/6+}$, $Cu^{2+/}Cu^{1+}$ or $Au^{1+/0}$ systems.

Scheme 3

The cyclooctyl radical, on reaction with O_2 or with a metal-peroxo intermediate species [M]-OOH, could form $CyOO^\bullet$ (peroxyl radical) or CyOOH, respectively. $CyOO^\bullet$ can also form CyOOH upon H-abstraction from H_2O_2,[22,25] and CyOOH can decompose to the final products (cyclooctanol and cyclooctanone). Moreover, metal-promoted decomposition of CyOOH could lead to the peroxyl ($CyOO^\bullet$) or the oxyl ($CyO^\bullet$) radical and cyclooctanol could then be formed by H-abstraction from cyclooctane by $CyO^\bullet$ or upon decomposition of $CyOO^\bullet$ to both cyclooctanol and cyclooctanone.[1g,1h,22,25]

Conclusions

We have found simple and convenient routes for the formation of water soluble dichloro-V (**1**), -Fe (**2**) and -Ni (**3**) complexes, and the full-sandwich Cu (**4**) compound, with the tri-hapto *N,N,N*-coordinated mode of 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate, thus contributing towards the expansion of the still scarcely explored coordination chemistry of such a type of C-functionalized scorpionate.

We have also showed the application of such a type of compounds as catalysts for the single-pot homogeneous cyclooctane oxidation, under mild conditions and with an environmentally friendly oxidant (H_2O_2). **4** provides the best activity which is promoted in acidic medium reaching remarkable yields (based on the alkane) up to *ca*. 27%.

Hence, the work also shows that a full-sandwich complex, such as **4,** can present a high catalytic activity, if sufficiently labile to form an active species.

The reactions proceed via radical mechanisms with involvement of both C-centred and O-centred radicals.

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FIGURE CAPTIONS

Figure 1

(a) Thermal ellipsoid diagrams of complex **4** with atomic numbering schemes. Ellipsoids are drawn at 30% probability and the sulfonate counter-ions are omitted. (b) Fragment of the crystal packing diagram (arbitrary view) of **4** showing the $\pi\cdots\pi$ contacts. Symmetry operation used to generate equivalent atoms: *i)* -x,1-y,-z; *ii*) 1-x,1-y,-z. Selected bond distances (Å) and angles (º): N11–Cu1 1.999(3), N14–Cu1 2.021(3), N17–Cu1 2.347(3), O11–S1 1.436(4), O12–S1 1.411(4), O13–S1 1.600(3), C1–C2 1.540(5), C2–O13 1.446(5), C3–S1 1.741(5), N11–Cu1–N14 86.20(13), N11–Cu1–N17 86.20(13), N14–Cu1–N17 84.19(12), N11–Cu1–N14^{i} 93.80(13), N11–Cu1–N17^{i} 99.52(12), N14–Cu1–N17^{i} 95.81(12).

Figure 2

Cyclic voltammograms of complex **1** initiated by the anodic sweep, at a Pt electrode, in 0.2 M $[^{n}Bu_4N][BF_4]/NCMe$ solution (v = 200 mVs^{-1}), * $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$.

Figure 3

Effect of reaction time on the overall (cyclooctanol + cyclooctanone) products yield for oxidation of cyclooctane catalysed by **1** – **4**. Reaction conditions are those of Table 3.

Figure 4

(a) Effect of HNO_3 in the oxidation of cyclooctane catalysed by **1**, **2** and **4** on the overall yield. Reaction conditions are those of Table 3. (b) Effect of pyridine in the oxidation of cyclooctane catalysed by **1** and **4** on the overall yield. Reaction conditions are those of Table 3.

SCHEME CAPTIONS

Scheme 1
Synthesis and schematic representation of compounds **1**–**4**.

Scheme 2
Cyclooctane oxidation to cyclooctyl hydroperoxide, cyclooctanone and cyclooctanol.

Scheme 3
A possible mechanism path for oxidation of cyclooctane with H_2O_2 as oxidant.

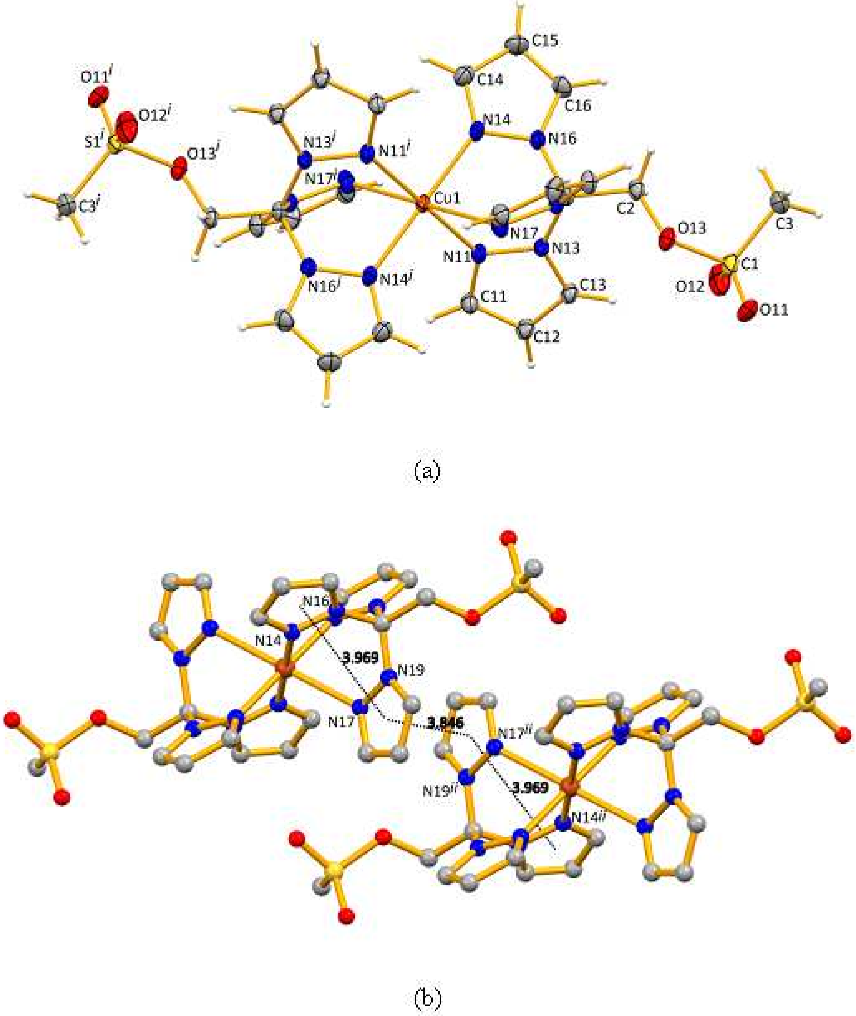

O11^i
O12^i
S1^i
O13^i
C3^i
N13^i
N11^i
N17^i
Cu1
N16^i
N14^i
C15
C14
C16
N14
N16
C2
N17
O13
C3
N11
N13
C1
O12
O11
C11
C13
C12
(a)
N16
N14
3.969
N19
N17
3.846
N17^{ii}
N19^{ii}
3.969
N14^{ii}
(b)

Figure 1

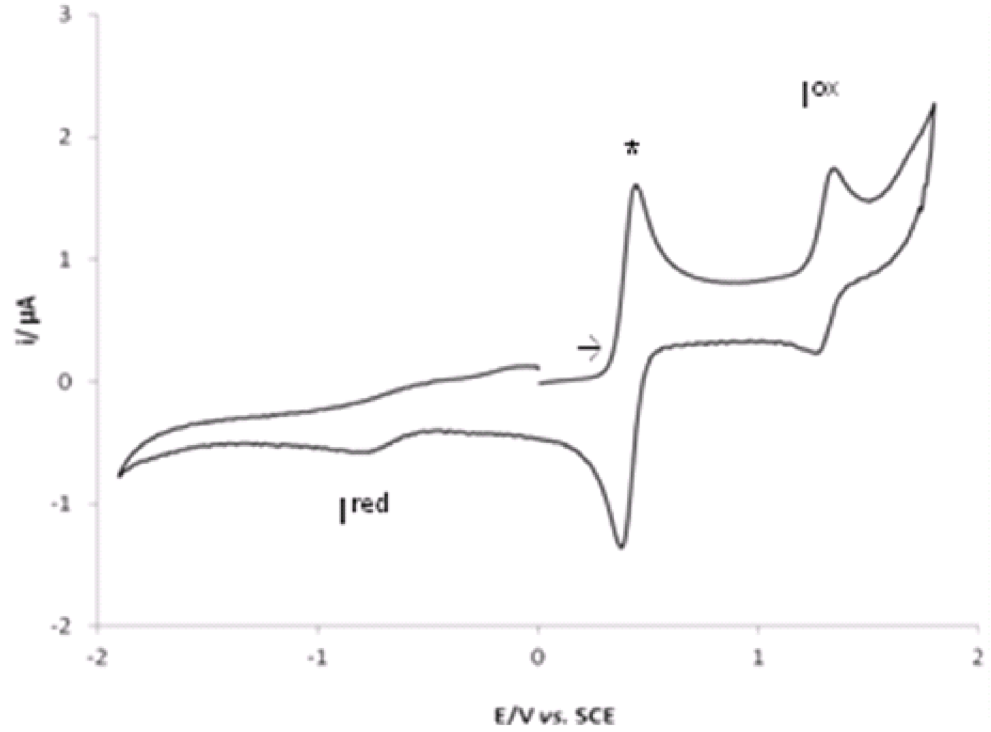
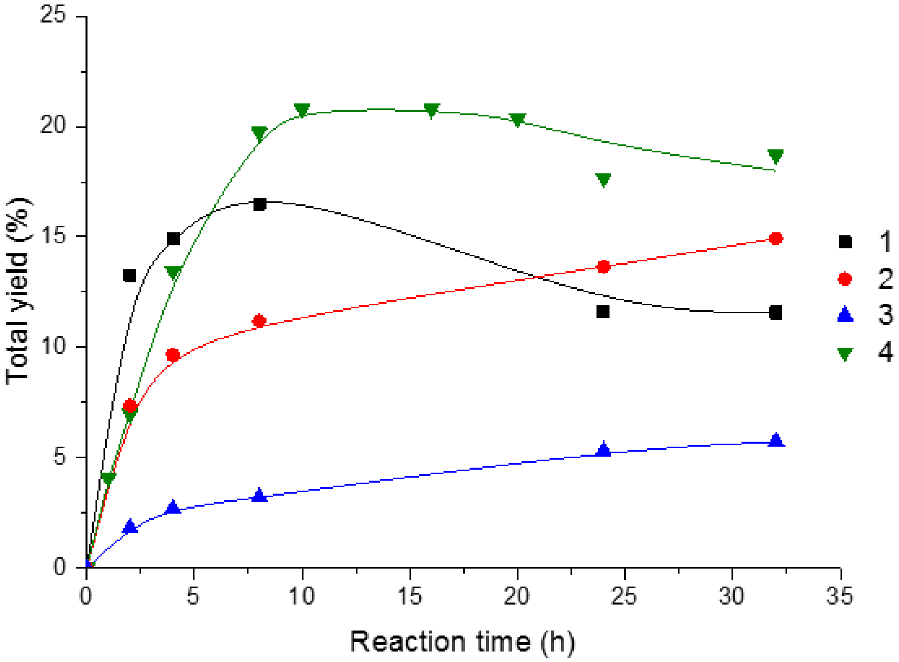


Figure 2



Total yield (%)
Reaction time (h)
0
5
10
15
20
25
0
5
10
15
20
25
30
35
■ 1
● 2
▲ 3
▼ 4

Figure 3

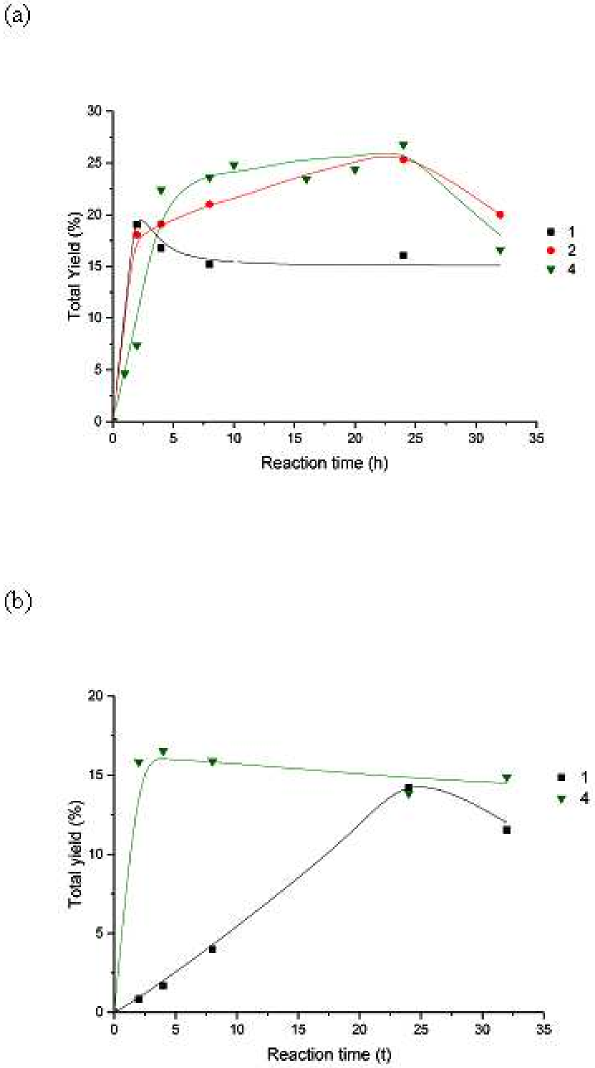
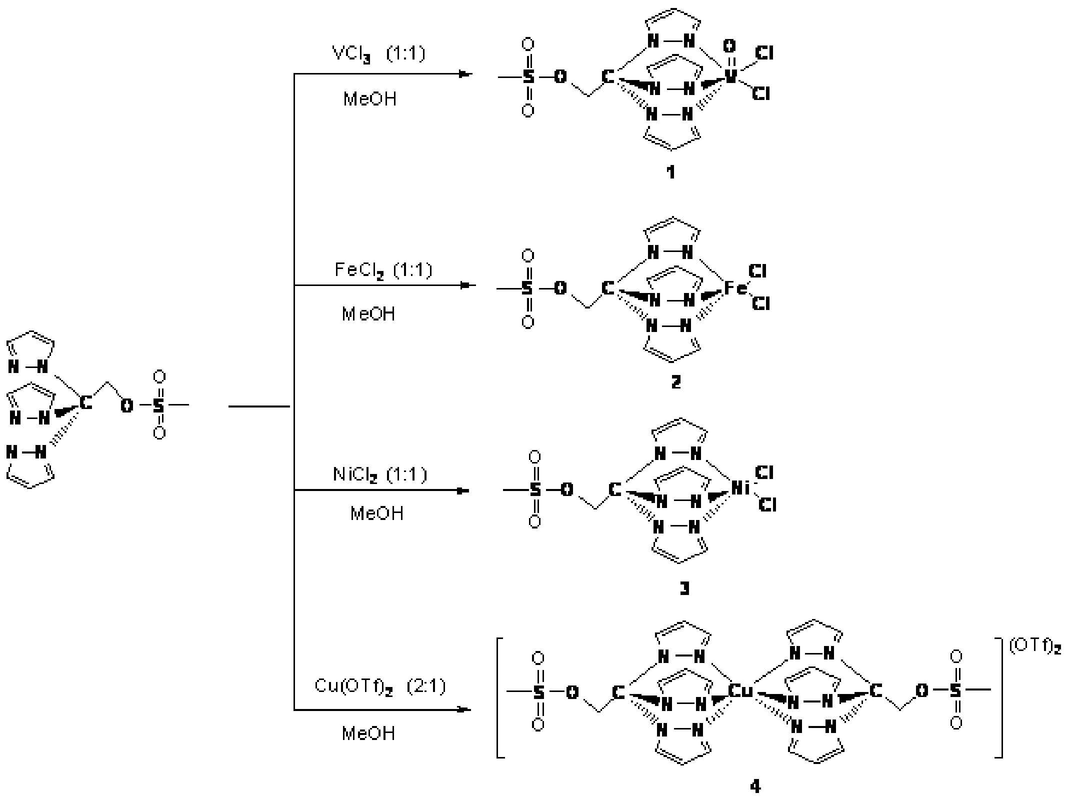
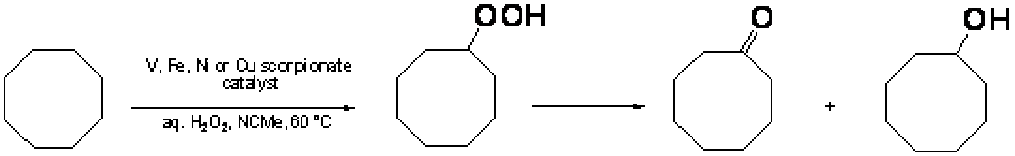

(a)
Total Yield (%)
0
5
10
15
20
25
30
Reaction time (h)
0
5
10
15
20
25
30
35
1
2
4
(b)
Total yield (%)
0
5
10
15
20
Reaction time (t)
0
5
10
15
20
25
30
35
1
4

Figure 4


VCl3 (1:1)
MeOH
FeCl2 (1:1)
MeOH
NiCl2 (1:1)
MeOH
Cu(OTf)2 (2:1)
MeOH
1
2
3
4
(OTf)2

Scheme 1



Scheme 2

$$\mathrm{HO^{\bullet} + CyH \longrightarrow H_2O + Cy^{\bullet}} \qquad (1)$$

$$\mathrm{Cy^{\bullet} + O_2 \longrightarrow CyOO^{\bullet}} \qquad (2)$$

$$\mathrm{CyOO^{\bullet} + H_2O_2 \longrightarrow CyOOH + HOO^{\bullet}} \qquad (3)$$

$$\mathrm{CyOOH + [M^{n}] \longrightarrow CyOO^{\bullet} + H^{+} + [M^{n-1}]} \qquad (4)$$

$$\mathrm{CyOOH + [M^{n-1}] \longrightarrow CyO^{\bullet} + HO^{-} + [M^{n}]} \qquad (5)$$

$$\mathrm{CyO^{\bullet} + CyH \longrightarrow CyOH + Cy^{\bullet}} \qquad (6)$$

$$\mathrm{2CyOO^{\bullet} \longrightarrow CyOH + Cy_{-H}{=}O + O_2} \qquad (7)$$

Scheme 3

Graphical abstract

New water-soluble scorpionate complexes were synthesized and applied as selective catalysts for cyclooctane oxidation in presence of basic or acid additives.