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Iron(III) chloride – benzotriazole adducts with trigonal bipyramidal geometry: Spectroscopic, structural and catalytic studies

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ABSTRACT

The reactions of FeCl₃ with benzotriazole (btaH), 1-methylbenzotriazole (Mebta), 5,6dimethylbenzotriazole (5,6Me2btaH) and 5-chlorobenzotriazole (5ClbtaH) were studied in non-polar solvents. The new solid complexes [FeCl₃(btaH)₂] (1), $[FeCl_3(Mebta)_2]$ (2), $[FeCl_3(5,6Me_2btaH)_2]$ (3) and $[FeCl_3(5ClbtaH)_2]^2(5ClbtaH)$ (4) have been isolated. The structures of the complexes have been determined by singlecrystal, X-ray crystallography. The structures of 1-4 consist of mononuclear, highspin 5-coordinate molecules; in addition, the crystal structure of 4 contains two lattice 5ClbtaH molecules per [FeCl₃(5ClbtaH)₂] unit. The coordinated benzotriazole molecules behave as monodentate ligands with their ligated atom being the nitrogen of the position 3 of the azole ring. The geometry at iron(III) is trigonal bipyramidal with the chlorido ligands occupying the equatorial sites. The crystal structures of the complexes are stabilized by stacking interactions and H bonds (for 1, 3 and 4 only). The new complexes were characterized by elemental analyses, magnetic susceptibilities at room temperature and spectroscopic (IR, far-IR, solid-state electronic UV/VIS/near-IR, ⁵⁷Fe-Mössbauer, EPR only for complex **4**) methods. All data are discussed in terms of the nature of bonding and the known structures. Complexes 1, 2 and 4 have been tested as homogeneous (MeCN) oxidation catalysts in the presence of the "green" H_2O_2 oxidant; they display moderate to high catalytic activity in the oxidation of several alkenes, cyclohexane and *n*-hexane, which is described in detail.

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1. Introduction

The continuous improvement of synthetic methodology in inorganic chemistry has already allowed us to see coordination chemistry entering a phase of creative, rather than investigative, character. The development of metal complexes for applications in medicine and catalysis, and the synthesis of molecular clusters and coordination polymers with exciting physical properties (magnetic, optical, ...) are clear examples of this new era.

The central "players" in coordination chemistry are the metal atoms/ions and the ligands. The proper use of old ligands and the design of new ones underlies much of modern coordination chemistry. Alfred Werner and his successors employed simple inorganic and organic ligands, e.g. NH₃, H₂O, Cl⁻, CO₃²⁻, en, ... Later, inorganic chemists started to use varieties of complex, polydentate ligands (polypodal open-chain ligands, cyclic ligands, crown ethers, cryptands, sepulchrates, ligands of unusual reach, calixarenes, biologically relevant ligands, ...) to achieve specific purposes. Today, the design and use of such polydentate ligands is an important frontier of research in contemporary inorganic chemistry [1].

A popular class of ligands consists of azoles and one family of them are benzotriazole (btaH) and its derivatives (Fig. 1). Over the last thirty years or so, we [2-18] and other groups [19-51] have been exploring the coordination chemistry of benzotriazoles. The first reason for this is the impressive anticorrosion activity of btaH and its benzene ring-substituted derivatives towards certain metals, particularly Cu and its alloys [52-55]. Chemical, physical and structural studies on realistic model metal complexes [23, 24] are needed to understand the complicated surface chemistry that leads to corrosion inhibition and to create better inhibitors than btaH. The second reason is the observation that the reactions between metal carboxylates or β -diketonates and btaH, its ring- (with non-donor groups) or its Nsubstituted (with donor groups) derivatives lead to incomplete replacement of the ancillary ligands by the deprotonated benzotriazoles and the formation of heteroleptic homonuclear or heteronuclear coordination clusters with novel structural motifs and interesting magnetic properties. For example, in previous reports, we have shown that the synthetic investigation of the [Ni(acac)₂(H₂O)₂]/btaOH and Ni(O₂CMe)₂ 4H₂O/btaOH reaction systems (acac is

the anion of 2,4-pentanedione and btaH is 1-hydroxybenzotriazole, i.e. R = OH and R' = H in Fig. 1) lead to complexes $[Ni_7(OH)_2(acac)_8(btaO)_4(H_2O)_2]$ [13] and [Ni₁₃(OH)₆(O₂CMe)₈(btaO)₁₂(H₂O)₆(*n*PrOH)₄] [18], respectively. The third reason is the capability of deprotonated benzotriazoles to form coordination polymers of various dimensionalities (depending on the benzotriazole coordination mode and the nature of the ancillary ligand present) with interesting photophysical and magnetic properties [10, 12, 15, 17, 34, 38, 40, 41, 43-45, 49]. Work from our groups includes the synthetic investigation of the Cu^{II}/btaOH/aqueous NH3 reaction system in MeOH which resulted in the solution of the 3D, diamond-like complex $[Cu(btaO)_2(MeOH)]_n$, which is a soft molecular magnet exhibiting two critical temperatures at 6.4 and 4.4 K [10] . Another reason for the intense interest in the coordination chemistry of btaH stems from its use as a bridging ligand in mixed organometallic/coordination compounds. For example, deprotonation of btaH by tris(cyclopentadienyl)dysprosium(III) has led to the dinuclear complex $[Dy_2(\mu-bta)_2(Cp)_4]$, a compound which exhibits single-molecule magnet behavior [56]. Finally, btaH is extremely useful in silver chemistry [37], because of its high affinity for Ag^I; this affinity has been the main reason of its successful use in conventional photographic systems for many years [57]. Complex $[Ag(bta)]_n$ has been reported to be an efficient silver source in black and white photothermographic (PTG) imaging systems [37]; more recently, it has been investigated as the silver source to be used in colour PTG materials designed for advanced photographic applications [58], compared to "conventional" PTG materials. Despite the extensive use of neutral and anionic benzotriazoles in 3dmetal chemistry, the number of Fe coordination complexes with benzotriazole or benzotriazolate ligation remains limited [4, 26, 29, 31, 33, 36, 39, 50]. Of particular interest are the Fe^{III}₁₄ clusters reported by McInnes, Brechin, Collison and co-workers [29, 39]; these complexes contain deprotonated bridging benzotriazoles, have high ground-state electronic spins of $S \le 25$ (among the highest known) and exhibit very large magnetocaloric effects. Moreover, no metal complexes of btaH, bta⁻ and its derivatives have been studied in catalysis to date. This work aims at the amalgamation of these two areas and reports FeCl₃benzotriazole adducts with remarkable activity as homogeneous catalysts for hydrocarbon oxidation using H_2O_2 as oxidant.



Fig. 1. The general structural formula of benzotriazoles. The parent member of this family of ligands is 1H-benzo[d][1,2,3]triazole or simply benzotriazole (btaH; R = R' = R'' = H). R and R' can be non-donor (Me, Cl, NO₂, ...) or donor (OH, COOH, CH₂OH, CH₂COOH, ...) groups. The ligands used in this work are btaH, 1-methylbenzotriazole (Mebta; R = Me, R' = R'' = H), 5-chlorobenzotriazole (5ClbtaH; R = H, R' = Cl, R'' = H) and 5,6-dimethylbenzotriazole (5,6Me₂btaH; R = H, R' = R'' = Me).

The development of efficient methods for hydrocarbon oxidation remains an important challenge for synthetic chemistry. For example, the selective transformation of inert C-H bonds of alkanes into useful functional groups has attracted much attention because alkanes are less expensive and more readily available than the current petrochemical feedstocks [59]. Moreover, the development of systems that achieve high selectivity using environmentally friendly processes and inexpensive oxidants represents a demand with direct ecological and financial benefits [60, 61]. Today there is an increased intense interest for the use of oxidants, like molecular O_2 and H₂O₂, which are environmentally friendly and do not give rise to any waste products [62]. It is also appreciated by industrial chemists that H₂O₂ is miscible with water and relatively easily to handle. Unfortunately, H₂O₂ can undergo radicalinduced decomposition to H₂O and O₂ by impurities and traces of metallic particles [63]. The direct oxidation of organic substrates by H_2O_2 is rare as the energy barrier for electron transfer from the substrate to the oxidant is usually high. However, nature has found methods to make controlled aerobic oxidations under highly mild conditions [64]. The remarkable increase in information on non-heme iron oxygenases within the past decade [65] has spurred efforts to explore the use of nonheme ligand scaffolds to facilitate such oxidation catalysis [66]. Detailed studies on biomimetic catalysts is of key importance for the design and development of novel,

efficient catalysts [67]. The use of an iron salt or complex and H₂O₂ traces back to the 19th century [68], but the major challenge has been to inhibit the homolytic cleavage of the peroxo O-O bond that produces non-selective, and thus unwanted, hydroxyl radicals [69]. Instead, the goal is to direct the metal-promoted cleavage towards the generation of a metal-based oxidant that can carry out hydrocarbon oxidations with high chemo-, regio- and stereoselectivity [69]. In this context, stereoselective hydroxylation, epoxidation and *cis*-dihydroxylation by iron biomimetic catalysts have been reported [70-78]. The most extensively studied oxidation catalysts thus far are complexes containing tetradentate N-donor ligands with configurations that allow two cis-orientated coordination sites to be available for peroxide binding and activation [72, 79, 80]. Involvement of macroacyclic N,O-donor ligands for the generation of non-heme iron-based catalysts has also been attempted [81-83]. However, new, efficient, low-cost and easy-to-prepare iron catalysts remain at high demand for hydrocarbon oxidation by H_2O_2 . We have thus decided to evaluate simple 5coordinate FeCl₃-benzotriazole complexes as homogeneous catalysts for hydrocarbon oxidation with H₂O₂ as oxidant; as it will be described, the complexes show remarkable effectiveness towards several substrates at room temperature.

2. Experimental

2.1. General information and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Patras (Greece) using an EA 1108 Carlo Erba analyzer. Conductivity measurements were carried out at 25 °C with a Metrohm-Herisau E-527 bridge and a cell of standard constant. IR spectra (4000-400 cm⁻¹) were recorded on a Perkin-Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. Far-IR spectra (400-50 cm⁻¹) were recorded on a Brucker IFS 113v FT spectrometer with samples prepared as polyethylene pellets. Solid-state (diffuse reflectance) electronic spectra (1500-350 nm) were recorded on a Perkin-Elmer 330 spectrophotometer using spectroscopic grade MgO as reference. Solution electronic spectra (850-330 nm) were recorded on a Varian 634 spectrophotometer.

Magnetic susceptibilities were measured at room temperature using the Faraday method and employing a Cahn-Ventron RM-2 balance standardized with HgCo(NCS)₄. Molar magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. ⁵⁷Fe Mössbauer spectra were recorded at room temperature with a conventional constant acceleration spectrometer; the γ -ray source used was ⁵⁷Co in a Rh matrix and the isomer shifts were referenced to metallic iron. The EPR spectrum of a powdered sample of [FeCl₃(5ClbtaH)₂]⁻²(5ClbtaH) was recorded at 4.2 K using a Bruker ER 200D spectrometer operating at X-band frequencies; the low temperature was obtained using an Oxford Instruments ESR cryostat.

2.2. Catalytic experiments

All substrates were purchased from Aldrich, in their highest commercial purity, stored at 5 °C and purified by passage through a column of basic alumina prior to use. A 30% aqueous solution of H₂O₂ was used as oxidant. For the catalytic evaluation, H₂O₂ (30%) diluted in MeCN (1:10 v/v) was slowly added (within a period of 10 min) to an MeCN solution of the iron(III) complex (the catalyst) and the substrate under an Ar atmosphere at room temperature (26 °C). Acetophenone or bromobenzene were used as internal standard. Catalytic reactions started by adding the oxidant into the reaction mixture. The catalyst : oxidant : substrate ratio was 1 : 20 : 1000 µmol for cyclohexene, 1-methylcyclohexene, cyclooctene, limonene, cyclohexane and *n*-hexane, and 1 : 50 : 1000 µmol for styrene, *trans-β*-methyl styrene and *cis*-stilbene. The total volume of the catalytic reaction solution was 1 ml. The large excess of the substrate was expected to minimize over-oxidation of oxidation products and to protect the catalyst from oxidative destruction. The oxidant was added slowly in order to minimize potential iron-catalyzed H₂O₂ decomposition *via* catalase activity.

The progress of the catalytic reaction was monitored using GC-MS by removing small samples of the reaction mixture. GC analysis was performed using a 8000 Fisons chromatograph with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer. The yields reported herein are based on the amount of H_2O_2 oxidant converted into oxygenated products. Reactions were complete within 6 h. In some cases, oxidations catalyzed by

 $[FeCl_3(5ClbtaH)_2]^2(5ClbtaH)$ were accomplished within 2 h (*vide infra*). To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of the commercially available compounds. Black experiments revealed that no oxidative reactions took place without the catalyst.

2.3. Compound preparation

2.3.1. [FeCl₃(btaH)₂] (1)

To an orange solution of btaH (0.119 g, 1.00 mmol) in CH₂Cl₂ (20 mL) was slowly added solid FeCl₃ (0.081 g, 0.50 mmol). Most of the solid soon dissolved. The resulting slurry was kept under stirring for 10 min, filtered and the yellow filtrate was stored at 5 °C in a closed flask. Well-formed, X-ray quality orange crystals of the product were deposited after 2 days. The crystals were collected by filtration, washed with cold CH₂Cl₂ (1 mL) and Et₂O (2x3 mL), and dried in air. Typical yields were in the 35-40% range. The yield can be increased up to \sim 70% using concentrated reaction mixtures (e.g. 4.0 mmol of btaH and 2.0 mmol of FeCl₃ in 25 mL of CH₂Cl₂), but in this case the product was isolated as a microcrystalline powder even at room temperature. Anal. Calc. for C₁₂H₁₀FeN₆Cl₃: C, 36.0; H, 2.5; N, 21.0. Found: C, 35.7; H, 2.6; N, 20.8%. Selected IR data (KBr, cm⁻¹): v = 3232s, 1622m, 1220m, 1112s, 1024m, 744s, 430m. Selected far-IR data (polyethylene, cm⁻¹): v = 374s, 215s. Molar conductivity, $\Lambda_{\rm M}$ (MeCN, 10⁻³ M, 25 °C): 4 S cm² mol⁻¹. $\Lambda_{\rm M}$ (MeNO₂, 10⁻³ M, 25 °C): 80 S cm² mol⁻¹. Effective magnetic moment, μ_{eff} : 5.79 BM at 24 °C. Solid-state electronic spectra (nm): $\lambda = 415, 606, 837, 1123, 1385$. ⁵⁷Fe Mössbauer data (mm s⁻¹, room temperature): $\delta = 0.37$, $\Delta E_{\rm O} = 0.56$.

2.3.2. [FeCl₃(Mebta)₂] (2)

To a colourless solution of Mebta (0.133 g, 1.00 mmol) in CHCl₃ (15 mL) was slowly added a green suspension of FeCl₃ (0.081 g, 0.50 mmol) in the same solvent (15 mL). The resulting orange slurry was stirred for 30 min and filtered. Overnight slow evaporation of the yellow filtrate at room temperature gave X-ray quality, yellow crystals of the product, which were collected by filtration, washed with cold CHCl₃ (1 mL) and Et₂O (3x3 mL), and dried in air. Typical yields were in the range 55-60%. *Anal.* Calc. for C₁₄H₁₄FeN₆Cl₃: C, 39.2; H, 3.3; N, 19.6. Found: C, 39.0; H, 3.4; N, 19.4 %. Selected IR data (KBr, cm⁻¹): v = 1618m, 1218s, 1136m, 750s, 432m.

Selected far-IR data (polyethylene, cm⁻¹): v = 378s, 196s. $\Lambda_{\rm M}$ (MeCN, 10⁻³ M, 25 °C): 6 S cm² mol⁻¹. $\Lambda_{\rm M}$ (MeNO₂, 10⁻³ M, 25 °C): 77 S cm² mol⁻¹. $\mu_{\rm eff}$: 6.06 BM at 20 °C. Solid-state electronic spectra (nm): $\lambda = 436$, 604, 837, 1137, 1345, 1379. ⁵⁷Fe Mössbauer data (mm s⁻¹, room temperature): $\delta = 0.24$, $\Delta E_{\rm Q} = 0.27$.

2.3.3. [FeCl₃(5,6Me₂btaH)₂] (3)

To an orange solution of 5,6Me₂btaH (0.216 g, 1.50 mmol) in CHCl₃ (10 mL) was added a green suspension of FeCl₃ (0.081 g, 0.50 mmol) in the same solvent (10 mL). The resulting slurry dissolved upon stirring and addition of MeOH (3 mL) to give a dark red solution, which was layered with *n*-hexane (40 mL). Slow mixing gave well-formed, X-ray quality red crystals of the product over a period of 3 days. The crystals were collected by filtration, washed with cold CHCl₃ (1 mL) and Et₂O (4x3 mL), and dried in air. Typical yields were in the 65-70% range (based on the Fe^{III} available). *Anal.* Calc. for C₁₆H₁₈FeN₆Cl₃: C, 42.1; H, 4.0; N, 18.4. Found: C, 42.4; H, 3.9; N, 18.1%. Selected IR data (KBr, cm⁻¹): v = 3244sb, 1586m, 1226s, 1100s, 1024m, 770m, 474w. Selected far-IR data (polyethylene, cm⁻¹): v = 378s, 214s. $\Lambda_{\rm M}$ (MeCN, 10⁻³ M, 25 °C): 3 S cm² mol⁻¹. $\Lambda_{\rm M}$ (MeNO₂, 10⁻³ M, 25 °C): 80 S cm² mol⁻¹. $\mu_{\rm eff}$: 6.01 BM at 26 °C. Solid-state electronic spectra (nm): $\lambda = 411$, 582, 895, 1097, 1369. ⁵⁷Fe Mössbauer data (mm s⁻¹, room temperature): $\delta = 0.25$, $\Delta E_Q = 0.30$.

2.3.4. [FeCl₃(5ClbtaH)₂]⁻2(5ClbtaH) (4)

To a colourless solution of 5ClbtaH (0.230 g, 1.50 mmol) in a solvent mixture comprising 20 mL CHCl₃ and 1.5 mL EtOH was added solid FeCl₃ (0.081 g, 0.50 mmol). The solid soon dissolved. The resulting dark orange solution was kept under stirring for 20 min and then layered with *n*-hexane (35 mL). Slow mixing gave well-formed, X-ray quality red crystals of the product over a period of 3 days. The crystals were collected by filtration, washed with cold EtOH (1 mL) and Et₂O (2x3 mL), and dried in air. The yield was ~70% (based on the ligand available). *Anal.* Calc. for C₂₄H₁₆FeN₁₂Cl₇: C, 37.1; H, 2.1; N, 21.7. Found: C, 36.8; H, 2.1; N, 21.3%. Selected IR data (KBr, cm⁻¹): v = 3260-2800sb, 1264m, 1202s, 1112m, 1070m, 942m, 804m, 432w. Selected far-IR data (polyethylene, cm⁻¹): v = 380s, 213s. $\Lambda_{\rm M}$ (MeCN, 10⁻³ M, 25 °C): 8 S cm² mol⁻¹. $\Lambda_{\rm M}$ (MeNO₂, 10⁻³ M, 25 °C): 81 S cm² mol⁻¹. $\mu_{\rm eff}$: 6.05 BM at 24 °C. Solid-state electronic spectra (nm): $\lambda = 394$, 610, 838, 1385. ⁵⁷Fe Mössbauer data (mm s⁻¹, room temperature): $\delta = 0.28$, $\Delta E_{\rm Q} = 0.28$. EPR data (solid state, 4.2 K):

g = 5.83, 1.89. The EPR spectrum of a frozen solution (4.2 K) of the complex in MeNO₂ is complicated; six transitions with g values in the 9.22-2.01 range are observed.

2.4. Single-crystal X-ray crystallography

A yellow crystal of **2** (0.05 x 0.14 x 0.30 mm) and red crystals of **3** (0.11 x 0.12 x 0.48 mm) and **4** (0.11 x 0.41 x 0.54 mm) were taken directly from the mother liquid and immediately cooled to 160 K. Diffraction measurements were performed on a Rigaku R-Axis SPIDER Image Plate diffractometer using graphite-monochromated Cu K α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction and empirical absorption correction) were carried out using the CrystalClear program package [84]. Data for a selected orange needle of **1** (0.05 x 0.05 x 0.15 mm) were collected at Station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, using a Bruker 08 diffractometer equipped with an ApexII CCD detector (synchrotron radiation of 0.77490 Å, silicon 111 monochromator, 100 K). The data were intergrated using the program SAINT v7.60A. A multi-scan correction for absorption was applied using the program SADABS-2008/1.

The structures of **2-4** were solved by direct methods using SHELXS-97 [85] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [86]. The H-atoms were located by difference maps and refined isotropically. All non-H atoms were refined anisotropically. In the structure of **4**, the chlorine atom of the coordinated ligand was found disordered and refined over two orientations with occupation factors summing one. The structure of **1** was solved by direct methods [85] and refined using the SHELX-TL suite of programs [87]. All carbon bonded H-atoms were affixed geometrically and refined as riding atoms with C-H = 0.95-0.99 Å and U_{iso}(H) = 1.2 times U_{eq}(C). The azole H-atom was located and refined freely. Important crystal data and parameters for data collection and refinement are listed in Table 1.

Table 1

Crystallographic data for complexes 1-4.

Parameter	1	2	3	4
				0
Empirical formula	$C_{12}H_{10}FeN_6Cl_3$	$C_{14}H_{14}FeN_6Cl_3$	C ₁₆ H ₁₈ FeN ₆ Cl ₃	$C_{24}H_{16}FeN_{12}Cl_7$
M (g mol ⁻¹)	400.46	428.51	456.56	776.49
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	C2/c	C2/c	P2/n	<i>P</i> 22 ₁ 2 ₁
<i>a</i> (Å)	18.385(2)	15.0523(2)	7.8454(1)	7.5066(1)
<i>b</i> (Å)	6.7661(7)	7.3248(1)	7.9152(1)	8.0738(1)
<i>c</i> (Å)	14.3770(16)	17.1315(3)	16.1391(2)	25.0627(4)
α (°)	90	90	90	90
eta (°)	121.667(3)	112.030(1)	100.633(1)	90
γ (°)	90	90	90	90
$V(\text{\AA}^3)$	1522.1(3)	1750.93(5)	985.00(2)	1518.97(4)
Ζ	4	4	2	2
$p_{\rm calc} ({\rm g \ cm}^{-3})$	1.748	1.626	1.539	1.698(2)
Radiation, λ (Å)	synchrotron, 0.77490	Cu Ka, 1.54178	Cu Ka, 1.54178	Cu Ka, 1.54178
<i>T</i> (K)	100(2)	160(2)	160(2)	160(2)
$2\theta_{\max}$ (°)	69.1	130.0	130.0	130.0
μ (mm ⁻¹)	1.919	11.200	9.992	9.997
F (000)	804	868	466	778
Total reflections	10613	9217	8343	13094
Unique reflections (R_{int})	2415 (0.0543)	1409 (0.0997)	1654 (0.0552)	2524 (0.0786)
Data with $I > 2\sigma(I)$	2215	1261	1565	2338
Parameters refined	105	126	155	233
$(\Delta \rho)_{\rm max}/(\Delta \rho)_{\rm min} ({\rm e}~{\rm \AA}^{-3})$	0.493 / -0.305	0.546 / -1.313	0.376 / -0.439	0.475 / -0.695
Goodness-of-fit (GOF)(on F^2)	1.018	1.113	1.091	1.049
$R_1^{a} (I \geq 2\sigma(I))$	0.0277	0.0495	0.0351	0.0441
$wR_2^{b,c} (I \geq 2\sigma(I))$	0.0751	0.1132	0.0912	0.1010

 $\overline{{}^{\mathbf{a}}R_{1} = \Sigma(|F_{o}| - |F_{c}|) / \Sigma(|F_{o}|)}.$

^b $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}.$

^c $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2) / 3$. a = 0.0378, b = 1.3396 for **1**; a = 0.0416, b = 5.5658 for **2**; a = 0.0442, b = 0.5039 for **3**; a = 0.0448, b = 0.4603 for **4**.

3. Results and discussion

3.1. Synthetic comments in brief

Complexes 1-4 are prepared readily by the direct reactions between almost anhydrous iron chloride(III) and the ligands in non-polar solvents or predominantly non-polar solvent mixtures in moderate to good yields. Their formation is summarized in Eqs. (1) and (2), where L = btaH, Mebta and 5,6Me₂btaH (Fig. 1).

(2)

The use of non-polar organic solvents, i.e. CH_2Cl_2 and $CHCl_3$, is reflected on the molecular (i.e. non-ionic) nature of the products. Employment of more polar solvents (e.g. alcohols) in FeCl₃/monodentate organic ligand reaction systems often leads to ionic complexes of the general formula [FeCl₂(monodentate ligand)₄][FeCl₄] [88,89]. The ligand to metal reaction molar ratio does not affect the identity of the products in the solvents used. Adducts **1-4** are the *only* products from the 1:1, 2:1, 3:1 and 4:1 reaction mixtures. For example, we wondered whether we could prepare a compound with the stoichiometry [FeCl₃(5ClbtaH)₂], similar to that in **1-3**. However, all our efforts failed; it seems that the incorporation of two lattice 5ClbtaH molecules is favoured by thermodynamic reasons.

4

3.2. Description of structures

Selected bond distances and angles for complexes **1-4** are listed in Tables 2-5. Partially labeled plots and aspects of the crystal (supramolecular) structures of the complexes are shown in Figs. 2-9. The structures of **1-3** consist of mononuclear [FeCl₃L₂] molecules (L = btaH, Mebta, 5,6Me₂btaH, while the structure of **4** consists of [FeCl₃(5ClbtaH)₂] species and lattice 5ClbtaH molecules in an 1:2 ratio. Since the molecules [FeCl₃(btaH)₂], [FeCl₃(Mebta)₂], [FeCl₃(5,6Me₂btaH)₂] and

 $[FeCl_3(5ClbtaH)_2]$ have similar structures, a general description will be given. The crystal structures of the compounds will be analyzed separately.



Fig. 2. Partially labeled plot of the molecular structure of **1**. Only the H atom of the azole ring is shown. Primes are used for symmetry-related atoms, see the footnote of Table 2. Note that the donor atom N(1) [and its symmetry equivalent] is the nitrogen atom of the position 3 in the IUPAC numbering of btaH (Fig. 1). Colour scheme: Fe^{III}, orange; Cl, green; N, blue; C, grey.(Colour online).

Table 2

Selected interatomic distances (Å) and angles (°) for complex 1.^a

Bond lengths			
Fe(1) - Cl(1)	2.240(1)	N(1) - N(2)	1.314(1)
Fe(1) - Cl(2)	2.220(1)	N(2) - N(3)	1.335(2)
Fe(1) - N(1)	2.169(1)		
Bond angles			
Cl(1)-Fe(1)-Cl(1')	114.1(1)	Cl(2)-Fe(1)-N(1)	88.5(1)
Cl(1)-Fe(1)-Cl(2)	122.9(1)	N(1)-Fe(1)-N(1')	177.0
Cl(1)-Fe(1)-N(1)	91.9(1)	N(1)-N(2)-N(3)	108.1(1)
Cl(1)-Fe(1)-N(1')	89.8(1)		

^a Symmetry operation to generate equivalent atoms: (') -x, y, 1/2-z.

The molecules [FeCl₃L₂] (L = btaH, Mebta, 5,6Me₂btaH, 5ClbtaH) possess a crystallographically imposed 2-fold axis of symmetry passing through the Fe^{III} and Cl(2) atoms in **1-3** (Figs. 2-4), and through the Fe^{III} and Cl(1) atoms in **4** (Fig. 5). The Fe^{III} center is surrounded by three terminal chloro (or chlorido) ligands and two nitrogen atoms from two planar monodentate benzotriazole ligands; the latter use the nitrogen of the position 3 of the azole ring (Fig. 1) as the donor atom [this atom is labeled as N(1) in the structure of **1**, see Fig.2]. The five donor atoms define a trigonal bipyramid around the metal center with the three chloro ligands in the equatorial plane and the two L nitrogens in the axial positions. Analysis of the shape-determining angles using the approach of Reedijk, Addison and co-workers [90] yield values of trigonality index, τ , of 0.90, 0.85, 0.91 and 0.99 for **1**, **2**, **3** and **4**, respectively ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively). Thus, the *tbp* geometries in **1-3** are slightly distorted, the distortions from the idealized D_{3h} symmetry occurring both in the three Cl-Fe-Cl angles and in the nonlinearity of the N-Fe-N group.



Fig. 3. Partially labeled plot of the molecular structure of **2**, with H atoms omitted. Primes are used for symmetry-related atoms, see the footnote of Table 3. Colour scheme: Fe^{III}, orange; Cl, green; N, blue; C, grey. (Coulor online).

Selected Interation	ine distances (11) ai	id angles () for complex	4.	
Bond lengths				
Fe - Cl(1)	2.212(1)	N(1) - N(2)	1.340(4)	
Fe - Cl(2)	2.215(2)	N(2) - N(3)	1.321(5)	
Fe - N(3)	2.178(3)			0
Bond angles			Q-	
Cl(1)-Fe-Cl(1')	114.9(1)	Cl(2)-Fe-N(3)	86.7(1)	
Cl(1)-Fe-Cl(2)	122.5(1)	N(3)-Fe-N(3')	173.4(2)	
Cl(1)-Fe-N(3)	90.7(1)	N(1)-N(2)-N(3)	108.0(4)	
Cl(1)-Fe-N(3')	92.9(1)			

Table 3

Selected interatomic distances (Å) and angles (°) for complex 2.^a

^a Symmetry operation to generate equivalent atoms: (') 1-x, y, 1/2-z.

The average Fe^{III}-Cl distances are 2.233(1), 2.213(2), 2.227(1) and 2.212(2) Å in **1**, **2**, **3** and **4**, respectively. These values compare well with the average values of 2.216(1) and 2.221(2) Å reported for complexes $[FeCl_3(4-cpy)_2](4-cpy= 4-cyanopyridine)$ [91] and $[FeCl_3(NMe_3)_2]$ [92], respectively; these two compounds are the only structurally characterized mononuclear *tbp* complexes of the general formula *trans*-[FeCl_3L_2], where L is a monodentate N-donor (the term *trans* is used to indicate that the L ligands occupy axial sites in the *tbp* arrangement). The lengths of the Fe^{III}-N bonds [2.169(1)-2.185(3) Å] do not differ significantly in the four complexes. The relatively long bond distances may be due [91] to atom-atom repulsions between the donor nitrogen atoms and the chloro ligands; the donor N^{III} Cl intramolecular distances vary from 3.015 to 3.183 Å and they are similar to the values observed in [FeCl_3(4-cpy)_2] [91] for which a long Fe-N bond distance was also found.



Fig. 4. Partially labeled plot of the structure of complex **3**, also showing the intermolecular H bonds (see text for details). Only the H atoms of the azole rings are shown, Symmetry operations: (') 3/2-x, y, 1/2-z; ('') 1-x, 1-y, z. Colour scheme: Fe^{III}, orange; Cl, green; N, blue; C, grey. (Colour online).

Table 4

Selected interatomic distances (Å) and angles (°) for complex 3.^a

Bond lengths			
Fe - Cl(1)	2.235(1)	N(1) - N(2)	1.333(3)
Fe - Cl(2)	2.210(1)	N(2) - N(3)	1.312(3)
Fe – N(3)	2.162(2)		
Bond angles			
Cl(1)-Fe-Cl(1')	120.8(1)	Cl(2)-Fe-N(3)	87.6(1)
Cl(1)-Fe-Cl(2)	119.6(1)	N(3)-Fe-N(3')	175.2(1)
Cl(1)-Fe-N(3)	90.2(1)	N(1)-N(2)-N(3)	107.8(2)
Cl(1)-Fe-N(3')	92.2(1)		

^a Symmetry operation to generate equivalent atoms: (') 3/2-x, y, 1/2-z.

Complexes 1-4 join a small family of structurally characterized *tbp* iron(III) complexes of the general formula $[FeCl_3(monodentate ligand)_2]$ [91-93], in which the monodentate ligands are in axial positions. In only two members of this family the monodentate ligands are N-donors [91,92], the two other members being complexes $[FeCl_3(PMe_3)_2]$ and $[FeCl_3(PPh_3)_2]$ [93].



Fig. 5. Partially labeled plot of the structure of complex **4**, also showing the intermolecular H bonds (see text for details). Only the H atoms of the azole rings are shown. Symmetry operations: (') x, 2-y, -z; ('') 1-x, 1/2+y, -1/2-z; (''') x, 1+y, z. Colour scheme: Fe^{III}, orange; Cl, green; N, blue; C, grey. (Colour online).

Table 5

Selected interatomic distances (Å) and angles (°) for complex 4.^{a,b}

Bond lengths			
Fe - Cl(1)	2.204(2)	N(2) - N(3)	1.316(4)
Fe - Cl(2)	2.216(1)	N(11) - N(12)	1.346(4)
Fe - N(3)	2.185(3)	N(12) - N(13)	1.308(5)
N(1) – N(2)	1.336(4)		
0			
Bond angles			
Cl(1)-Fe-Cl(2)	120.6(1)	Cl(2)-Fe-N(3')	89.4(1)
Cl(2)-Fe-Cl(2')	118.7(1)	N(3)-Fe-N(3')	179.9(2)
Cl(1)-Fe-N(3)	90.0(1)	N(1)-N(2)-N(3)	107.3(3)
Cl(2)-Fe-N(3)	90.6(1)	N(11)-N(12)-N(13)	107.9(3)

^a Symmetry operation to generate equivalent atoms: (') *x*, 2-*y*, -*z*.

^b Atoms N(11), N(12) and N(13) belong to the uncoordinated, i.e. lattice 5ClbtaH molecule.

The crystal structure of **1** is stabilized by intermolecular H bonds and π - π stacking interactions. The [FeCl₃(btaH)₂] molecules form 1D chains as a consequence of the N(3)-H(N3)^{...}Cl(1') H-bonding scheme; the dimensions of this intermolecular H bond are: N(3)^{...}Cl(1') = 3.246 Å, H(N3)^{...}Cl(1') = 2.397 Å, N(3)-H(N3)^{...}Cl(1') =

158.2 °. The π - π interactions (Fig. 6) in this compound concern the stacking of the btaH molecules, which occurs in the direction of the *b* axis. Due to the 2-fold symmetry that generates the full coordination sphere of Fe(1), the benzotriazole ligands are not co-planar. They are canted by 6.45(1) °, with a centroid-to-centroid distance of 3.768 Å. Due to the canting of the ligands, the shift distance alternates between 1.553 and 1.776 Å. When the two rings that make up the btaH ligand are considered separately, it is clear that the triazole ring makes one closer interaction with the benzene ring (3.546 Å) and one longer (3.789 Å).



Fig. 6. The stacking interactions in complex 1.

The lattice structure of **2** is built through intermolecular π - π stacking interactions between the Mebta ligands (Fig. 7). Each [FeCl₃(Mebta)₂] molecule interacts with four of its neighbors. The mean planes defined by atoms N(1)-C(9) and N(1')-C(9') [(') = 1-x, 1-y, -z] are parallel with an interplanar distance of 3.794 Å (green dashed lines) and these defined by N(1)-C(9) and N(1'')-C(9'') [('') = 1-x, -y, -z] are also parallel with an interplanar distance of 3.782 Å (red dashed lines). The so-formed 2D network of **2** extends parallel to the *bc* plane.



Fig. 7. A small part of the 2D lattice structure of **2** due to π - π stacking interactions (dashed lines); see text for details. (Colour online).

The crystal structure of complex 3 is stabilized by intermolecular π - π stacking interaction between the 5,6Me₂btaH ligands of neighboring molecules (Fig. 8a) as well as H bonding interactions (Figs. 4 and 8b). The ligands defined by atoms N(1)-C(9) and their symmetry equivalents through the operation 2-x, 1-y, -z are parallel with an interplanar distance of 3.530 Å (red dashed lines). Moreover, the benzene rings defined by atoms C(4)-C(9) and their symmetry equivalents through the operation 2-x, -y, -z are also parallel to each other with an interplanar distance of 4.322 Å (green dashed lines). These two types of π - π interactions (one strong, the other weak) build the 2D structure of the complex which extends parallel to the (101) plane (Fig. 8a). The layers are further linked through H bonds, creating the 3D lattice structure of **3**. Each [FeCl₃(5,6Me₂btaH)₂] unit links to two neighboring molecules through two weak N(1)-H^{...}N(2) H bonds as shown in Fig. 4 $[N(1)^{...}N(2)(1-x, 1-y, -z)]$ = 2.886 Å, $H(N1)^{\dots}N(2)(1-x, 1-y, -z) = 2.357$ Å, N(1)- $H(N1)^{\dots}N(2)(1-x, 1-y, -z) =$ 124.0°]. In Fig. 4 only one neighboring molecule is shown; the other has been omitted because it is obviously created at the other side of the molecule by the 2-fold axis possessed by the molecule. Fig. 8b shows three layers linked through N-H."N interactions (orange lines) which build the 3D network of the complex.



Fig. 8. (a) A small part of the 2D network of **3** created by the combination of strong and weak π - π stacking interactions (red and green dashed lines). (b) A small part of the 3D network of the complex formed by N-H^{...}N interactions (orange lines) between molecules of different layers. See text for details. (Colour online).

The lattice structure of **4** is built through two types of π - π stacking interactions (Fig. 9). The coordinated 5ClbtaH ligand defined by atoms N(1)-C(9) and the lattice 5ClbtaH molecule defined by atoms N(11)-C(19) are connected through π - π interactions; the two mean planes form an angle of 3.37 ° with an interplanar distance of 3.544 Å (red dashed lines). A second type of π - π interactions between the benzene rings defined by atoms C(4)-C(9) and C(14)-C(19) [through the symmetry operation - 1+x, y, z] is responsible for the 1D lattice structure which extends parallel to the a axis; the two mean planes form an angle of 3.27 ° with an interplanar distance of

3.750 Å (green dashed lines). The chains further link through H bonding interactions to generate the overall 3D network of **4**. The dimensions of the H bonds are: $N(1)^{\dots}N(13) [1-x, 1/2+y, -1/2-z] = 2.826$ Å, $H(N1)^{\dots}N(13) [1-x, 1/2+y, -1/2-z] = 2.005$ Å, N(1)-H(N1)^{\dots}N(13) [1-x, 1/2+y, -1/2-z] = 144.4°; $N(2)^{\dots}N(11) [x, 1+y, z] = 3.054$ Å, $H(N11) [x, 1+y, z]^{\dots}N(2) = 2.323$ Å, N(11) [x, 1+y, z]-H(N11) $[x, 1+y, z]^{\dots}N(2) = 143.4$ Å. Each [FeCl₃(5ClbtaH)₂] molecule interacts through H bonds with four lattice 5ClbtaH molecules belonging to neighboring chains. In Fig. 5 only two lattice 5ClbtaH molecules belonging to a neighboring chain and lying at one side of [FeCl₃(5ClbtaH)₂] are shown; the other have been omitted because they are obviously created at the other side of the molecule by the 2-fold axis possessed by [FeCl₃(5ClbtaH)₂].



Fig. 9. A small part of the 1D lattice structure of complex 4 created by π - π stacking interactions; see text for details. (Colour online).

3.3. Physical and spectroscopic characterization

Data have been given in Part 2.3 (*vide supra*). A brief discussion will be presented here. Conductivity measurements for ~10⁻³ M solutions of **1-4** at 25 °C indicated the complexes to be non-electrolytes in MeCN ($\Lambda_M = 3-8 \text{ S cm}^2 \text{ mol}^{-1}$) [94]. Somewhat to our surprise, the Λ_M values in MeNO₂ (77-81 S cm² mol⁻¹) suggest that the compounds behave as 1:1 electrolytes in this solvent [94].

The IR spectra of **1**, **3** and **4** exhibit a band at 3232, 3244 and 3260-2800 cm⁻¹, respectively, assignable [21] to v(NH); the broadness and relatively low wavenumber of this band are both indicate of hydrogen bonding. In the spectra of **1-4** the bands due to v(N=N) and v(N-N) appearing at 1218-1264 and 1100-1136 cm⁻¹, respectively, are shifted to higher frequencies compared with those of the free ligands (1197-1212 and 1078-1110 cm⁻¹, respectively). For example, the IR spectrum of free Mebta exhibits two bands at 1197 and 1110 cm⁻¹ associated with the v(N=N) and v(N-N) modes of vibration, respectively [14]. These bands are shifted to 1218 and 1136 cm⁻¹, respectively, in the spectrum of **2**. Such shifts to higher frequencies are compatible with N(3) [Fig. 1] being the donor atom to the metal ion [2,3,9,14,21]. The appearance of two v(N=N) [1264, 1202 cm⁻¹] and two v(N-N) [1112, 1070 cm⁻¹] modes in the IR spectrum of **4** reflects the presence of both coordinated and uncoordinated 5ClbtaH molecules in its structure.

The far-IR spectra of **1-4** show one strong, terminal Fe^{III}-Cl stretch, v(Fe-Cl)_t, at 374-380 cm⁻¹ [91,93] and one weaker Fe^{III}-N stretching mode, v(Fe-N), at 196-215 cm⁻¹ [95]. A reasonable approximation of the molecular symmetry around Fe^{III} in the complexes is D_{3h} , and thus [91,95] one v(Fe-Cl)_t (E') and one v(Fe-N) (A₂'') would be expected. The wavenumbers of the v(Fe-Cl)_t vibration in **1-4** compare very well with the wavenumber of this mode reported for the *tbp* complex [FeCl₃(4-cpy)₂] [91].

The experimental μ_{eff} values of **1-4** at room temperature are in the range 5.79-6.06 BM, indicating a high-spin (S = 5/2) state and supporting a d_{xz}^{-1} , $d_{yz}^{-1} < d_{xy}^{1} d_{x2}$. $y_{2}^{-1} < d_{z2}$ electronic structure [93].

The solid-state electronic (diffuse reflectance) spectra of **1-4** exhibit four to five bands in the 550-1500 nm region, and a band at 394-436 nm; the wavelength of the latter and the fairly oxidizing nature of Fe(III) are suggestive of ligand-to-metal charge transfer character [96]. The bands in the 550-1500 nm region have their origin in spin-forbidden d-d transitions from the ground sextet state to the quartet levels [91,97]. The solution spectra (MeCN) of the complexes, recorded in the 350-800 nm region, are identical with the solid-state spectra.

Zero-field Mössbauer spectra of polycrystalline samples of 1-4 were measured at room temperature. The spectrum of 3 is shown in Fig. 10. The Mössbauer spectral parameters listed in the experimental section have been obtained from least-squares fit to the experimental points assuming Lorentzian absorption lines. The spectra consist of a single quadrupole-split doublet with no evidence of iron contaminants. The

isomer shift value δ (0.24-0.37 mm s⁻¹) is within the range expected for high-spin iron(III) in a non-sulfur environment [98-100]. The relatively low δ values may suggest 5-coordinate iron(III) complexes [100-102]. A relatively narrow half-line width (ca. 0.2 mm s⁻¹) is observed indicating that only one type of iron site is present [103]. The asymmetry in peak intensity at room temperature is typical of high-spin ferric complexes that have a large positive zero-field splitting parameter, *D* [104]; this phenomenon has been interpreted by Blume in terms of a temperature-dependent spin-spin relaxation time [105].



Fig. 10. Mössbauer spectrum of $[FeCl_3(5,6Me_2btaH)_2]$ (3) in zero applied field at room temperature.

The X-band EPR spectrum of complex $[FeCl_3(5ClbtaH)_2]^2(5ClbtaH)$ (4) has been recorded at 4.2 K in the solid state (Fig. 11 α) and in frozen MeNO₂ (Fig. 11 β). The solid-state spectrum exhibits a signal at $g \perp = 5.83$, typical of the perpendicular component in a tetragonal high-spin Fe(III) [93]. For a pure axial symmetry (E = 0) and a D value much greater than the microwave quantum, signals with $g \perp \approx 6$ and $g \approx$ 2 are expected [93]. We do not observe a signal at $g \approx 2$ that can be attributed to a parallel component, but this probably overlaps with the stronger signal at $g_{eff} = 1.89$. Considering the axial symmetry of this compound, proved by its structure, we can assume that E will be close to 0. According to the classical study of Dowsing and Gibson [106], five transition should be observed for small D; the $1/2 \rightarrow -1/2$ transition is expected to be nearly isotropic, but the other two (two at higher field, two at lower)

should be anisotropic with observable perpendicular and parallel components. Since we do not observe signals at g < 1.89 (up to a magnetic field of 12000 G), an examination of Figure 1 in ref. [106] suggests a *D* value larger than 0.2 cm⁻¹ for **4**.

The spectrum of **4** in MeNO₂ at 4.2 K is different compared with that in the solid state, suggesting that the *tbp* structure is not retained in solution. Six transitions are observed with g values in the 9.22-2.01 range. The high-field signal at g = 2.01 is assigned to the tetrahedral [FeCl₄]⁻ ion, while the remaining spectrum may be due to an octahedral species with small D and axial symmetry [93]. We tentatively propose that the decomposition of **4** takes place according to Eq. (3). This hypothesis is consistent with molar conductivity data which show that complex **4** is an 1:1 electrolyte in MeNO₂.





Fig. 11. X-band EPR spectrum of complex 4 in the solid state (α) and in MeNO₂ (β) at 4.2 K.

3.4. Catalytic studies

3.4.1. Hydrocarbon oxidation by complexes 1, 2 and 4

The catalytic properties of 1, 2 and 4 have been evaluated for hydrocarbon oxidation with H_2O_2 as oxidant. The substrates are shown in Fig. 12. The oxidation reactions were carried out at room temperature in an Ar atmosphere as detailed in the experimental section (Part 2.2). The reactions were usually complete within 6 h. Interestingly, when [FeCl₃(5ClbtaH)₂]²(5ClbtaH) (4) was used as catalyst, 1-methyl-cyclohexene and cyclohexane oxidations were accomplished within 2 h. The obtained catalytic results are summarized in Table 6. Fig. 13 provides a histogram plot of the data included in Table 1, while the time-depended cyclohexene oxidations catalyzed by the three complexes are shown in Fig. 14.



Fig. 12. The substrates used for oxidation reactions catalyzed homogeneously by complexes 1, 2 and 4 with H_2O_2 as oxidant.



Fig. 13. Distribution of oxidation products from reactions catalyzed by complexes 1, 2 and 4 in MeCN in the presence of H_2O_2 . See Table 6 for further details. (Colour online).

Table 6

Hydrocarbon oxidations catalyzed by complexes 1, 2 and 4 using H_2O_2 in MeCN under Ar.

Substrate	Products	[Fe	$eCl_3(btaH)_2](1)$	[FeCl ₃ ($[Mebta]_2] (2) \qquad [Fee$	$Cl_3(5ClbtaH)_2 2($	5ClbtaH) (4)
		Yield (%)	Total yield (%)	Yield (%)	Total yield (%)	Yield (%)	Total yield (%)
Cyclohexene ^a	cis-epoxide	22.4		6.0		20.0	
	2-cyclohexenol	27.0		26.0		26.0	
	2-cyclohexenone	22.0		16.0		25.0	
	cyclohexanediol	5.0		-		5.0	
			76.4 [°]		48.0 °		76.0 ^d (80.0) ^c
1-methyl-cyclohexene ^a	<i>cis</i> -epoxide	31.7		23.7		32.0	
	1-methyl-2-cyclohexen-1-ol	25.9		27.0		27.5	
	3-methyl-2-cyclohexen-1-ol	23.6		19.2		16.3	
	3-methyl-2-cyclohexen-1-one	18.4		20.6		24.2	
			99.6 °		90.5 °		100.0 ^d
Cyclooctene ^a	cis-epoxide	60.0		52.0		42.0	
2	2-cyclooctenone	4.0		-		-	
	,		64.0 ^c		52.0 °		42.0 ^d (48.5) ^c
Limonene ^a	cis-1,2-epoxide	14.8	\sim	10.3		16.6	
	trans-1.2-epoxide	12.9		9.2		10.0	
	cis-8,9-epoxide	4.0		2.9		5.0	
	trans-8.9-epoxide	3.5		2.6		4.0	
	limonene alcohol ^e	$11.2^{\rm f}$		10.8 ^g		14.3 ^h	
	limonene ketone ⁱ	5.0		5.1		10.0	
			51.4 °		40.9 °		57.4 °
Styrene ^b	epoxide	8.0		6.2		11.8	
	phenyl acetaldehyde	2.0		1.0		2.3	
	benzaldehyde	36.8		36.0		25.5	
			46.8 °		43.2 °		39.6 °
<i>Trans-β</i> -methyl-styrene ^b	trans-epoxide	30.0		14.5		32.0	
, , ,	methyl-benzyl alcohol	-		-		3.0	
	methyl-benzyl ketone	1.9		5.0		-	
	GGT		27				

		ACCEPT	ED MANUS	CRIPT			
	benzaldehyde	45.5	77.4 [°]	30.8	50.3 °	31.0	66.0 °
Cis-stilbene ^b	cis-epoxide	5.2		3.3		6.7	
	trans-epoxide	10.0		2.0		13.0	
	stilbene ketone	-		3.7		2.4	
	benzaldehyde	24.5		14.3		30.0	
			39.7 °		23.3 °		52.1 ^c
Cyclohexane ^a	cyclohexanol	26.3		13.7		27.0	
-	cyclohexanone	15.0		12.9		14.0	
	4-hexen-1-ol	3.0		7.2		1.8	
			44.3 °		33.8 °		42.8 ^d (42.8) ^c
<i>n</i> -hexane ^a	3-hexanone	4.5		2.3	0-	5.8	
	2-hexanone	4.0		2.9		5.6	
	3-hexanol	4.8		3.0	1	6.4	
	2-hexanol	-		2.0		4.8	
	1-hexanol	8.2				3.3	
			21.5 °		10.2 °		25.9 ^d (29.7) ^c
^a Conditions	s: ratio of catalyst : H ₂ O ₂ : substr	rate = 1 : 20 : 1000 in	n MeCN.				
^b Conditions	s: ratio of catalyst : H ₂ O ₂ : subst	rate = $1:50:1000$ in	n MeCN.				
^c The reaction	on was completed within 6 h.						
^d The reaction	on was completed within 2 h.						

^e Limonene alcohols were found to be a mixture of 1-ol and 6-ol.

^f The 11.2 % yield corresponds to 2.5% for 1-ol and 8.7% for 6-ol.

^g The 10.8 % yield corresponds to 3.8% for 1-ol and 7.0% for 6-ol.

^h The 14.3 % yield corresponds to 4.3% for 1-ol and 10.0% for 6-ol.

ⁱ The only observed ketone is the 6-one.



Fig. 14. Time dependence of cyclohexene oxidation catalyzed by complexes 1 (red line), 2 (black line) and 4 (green line) in MeCN with H_2O_2 as oxidant. (Colour online).

Based on Table 6, the present non-heme iron(III) catalysts are efficient in alkene oxidations providing significant yields. More specifically, cyclohexene oxidation catalyzed by complexes **1**, **2** and **4** provided oxidation products with combined yields of 76.4, 48.0 and 80.0 %, respectively within 6 h. It is worth mentioning that cyclohexene oxidation by **4** showed a 76.0 % yield only after 2 h (Figs. 14 and 15). Cyclohexene undergoes mainly allylic oxidation forming 2-cyclohexene-1-ol and 2-cyclohexene-1-one. However, cyclohexene epoxidation was also observed with low to moderate yields. In cyclohexene oxidation catalyzed by **1** and **4**, cyclohexanediol was also detected (5.0 %).



Fig. 15. Hydrocarbon oxidation yields obtained within 2 or 6 h using complex 4 as a homogeneous (MeCN) catalyst in the presence of H_2O_2 . (Colour online).

The methyl derivative 1-methyl-cyclohexene is more reactive in both epoxidation and allylic oxidation. Total yields in the 90.5-100.0% range have been observed by the present catalytic systems. Moreover, the complete association of H₂O₂ to cyclohexene oxidation products by complex 4 was achieved within 2 h. Cyclooctene as substrate afforded a singleproduct reaction giving only the cis-cyclooctene epoxide with yields 52.0 and 48.5% when 2 and 4 were used as catalysts, respectively. However, the use of 1 provided 60% epoxide and 4.0% 2-cyclooctenone. Generally, cyclooctene undergoes more readily epoxidation than allylic oxidation [83], but the over-oxidized 2-cyclooctenone derived from allylic oxidation was also observed using 1. The products detected from limonene oxidations were: (i) Two epoxides (cis and *trans*) originating from epoxidation of the electron-rich double bond in the 1,2-position; (ii) two epoxides (diastereoisomers) resulting from epoxidation of the more accessible, but less electron-rich, double bond at the 8,9-position; (iii) alcohols derived from hydroxylation of the double bond at the 1-position and from hydroxylation at the 6-position close to the 1,2-double bond; and (iv) amounts of the corresponding ketone at the 6-position. Styrene oxidation provided benzaldehyde as the major product derived by oxidative cleavage of the exo-cyclic double bond; however, epoxide and phenyl acetaldehyde have been also formed by direct oxidation of the same double bond. Overall, styrene was oxidized by 1, 2 and 4 with total

oxidation yields of 46.8, 43.2 and 39.6%, respectively. The methyl-substituted derivative *trans*- β -methyl styrene is more reactive than styrene giving total oxidation yields of 77.4, 50.3 and 60.0% by **1**, **2** and **4**, respectively. The identified products were the corresponding *trans*-epoxide and benzaldehyde as oxidation cleavage adducts. In some cases, methyl-benzyl alcohol and methyl-benzyl ketone were also detected. In the oxidation of *cis*-stilbene, the major product was benzaldehyde (an oxidative cleavage product); amounts of *cis*- and *trans*-stilbene epoxide, as well as stilbene ketone, were also detected.

Cyclohexane oxidation gave cyclohexanol and cyclohexanone with yields 26.3/15.0%, 13.7/12.9% and 27.0/14.0% for the **1**, **2** and **4** catalysts, respectively. However, small (**1**, **4**) or moderate (**2**) amounts of 4-hexen-1-ol have been also detected. These data give a total catalytic cyclohexane oxidation yield of 44.3 (**1**) and 33.8% (**2**) within 6 h, and 42.8% (**4**) within 2 h (Fig. 15). These total yields are much higher than the total yield reported (12.2%) for cyclohexane oxidation (under identical conditions) using complex [Fe^{III}Cl(L)], where L²⁻ is the dianion of 3-{2-[2-(3-hydroxy-1,3-diphenyl-allylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propen-1-ol [83]. The corresponding alcohol/ketone (A/K) ratio was found to be 1.95, 1.62 and 2.06 for **1**, **2** and **4**, respectively. The A/K ratio in cyclohexane oxidation can be used as a criterion of the presence and lifetime of free alkyl radical intermediates [107] as follows: (i) When A/K = 1, it assumes that the alkyl radicals are long-lived with a strong tendency to interact with O₂ to form alkyl-peroxy radicals [108]. At the end, following a Russell-type terminal stage [109], recombination of these radicals results in the formation of equimolar amounts of alcohol and ketone [70,107]; (ii) when A/K > 1, the radical 'OH is formed by a metal-based system and the metal center reacts directly to form the corresponding alcohol.

Finally, *n*-hexane oxidation by **1**, **2** and **4** gave 2- and 3-hexanone, as well as 3-, 2- and 1-hexanol with combined yields of 21.5, 10.2 and 29.7%, respectively. As far as we know, iron(III) complexes have never been reported as homogeneous catalysts in the oxidation of *n*-hexane.

3.4.2. Catalysts' stability

The efficiency and stability of the present Fe^{III} catalysts under operating conditions were studied by progressive addition of H_2O_2 to cyclohexane in MeCN. The starting catalyst : H_2O_2 : substrate molar ratio was 1 : 20 : 1000. After the end of each oxidation reaction, i.e. after 2 h, an additional amount of 20 equivs of H_2O_2 was added. The results are presented in Fig. 16. According to Fig. 16, in the oxidation reaction catalyzed by **4**, the first 20 equivs of H_2O_2 resulted in 42.8% cyclohexane oxidation. The addition of a second dose of 20 equivs of

the oxidant caused a yield increase to 57.5%. Third addition of H_2O_2 improved slightly the total oxidation to 63.3% and a fourth one to 67.8%. Overall, the data in Fig. 16 indicate that the evolution of the reaction catalyzed by complex **4** has practically stopped during the second run. This is probably due to catalyst destruction.



Fig. 16. Cyclohexane oxidation catalyzed by complex **4** in MeCN upon progressive addition of H_2O_2 . (Colour online).

3.4.3. Comments on the catalytic studies

The above described data can be summarized as follows: (i) Catalysts 1, 2 and 4 are capable of hydrogen abstraction and oxygen transfer in a variety of alkene substrates in MeCN using H_2O_2 as oxidant, resulting in significant yields of epoxidation and allyl oxidation products. (ii) Remarkable effectiveness has been observed towards cyclohexane oxidation with A/K values well above 1. (iii) Comparison of the three homogeneous catalysts shows that complexes 1 and 4 provide higher conversions than 2. Catalyst 4 is more reactive than 1, since some reactions studied herein were completed within 2 h, instead of the 6 h period required for reactions catalyzed by 1. Taking into account that the three Fe^{III} complexes have similar structures and probably do not dissociate in MeCN, the observed catalytic differences could be related to the different substituents on the azole and benzene rings, i.e. to electronic effects. The observed difference in reactivity implies the generation of a metal-based oxidant that could be

associated to carry out the catalytic oxidations. Although we are far from elucidating the mechanism of the catalytic reactions described in this work, preliminary data based on in-situ UV/VIS and EPR experiments suggest that the present non-heme Fe^{III}/H₂O₂ system does not follow a unique mechanistic path in MeCN, and the participation of two active oxidizing species (tentatively proposed to be Fe^v=O and Fe^{iv}=O/OH) can not ruled out [110]. Of particular mechanistic importance seems to be the observation that MeCN converts a large fraction of the Fe^{III} centers present in 1, 2 and 4 to the low-spin state (S = 1/2) by MeCN ligation [83,110]. ŞÚ

4. Conclusions and perspectives

The present work extends the body of results that emphasize the ability of benzotriazoles to form interesting structural types in 3d-metal chemistry. Our study has shown that the reactions of iron(III) chlorides with btaH and three of its derivatives lead to 1:2 adducts as the only products. Complexes 1-4 are new members of the extremely small family of mononuclear iron(III) complexes that exhibit a trigonal bipyramidal coordination geometry with exclusively monodentate ligands. The complexes have interesting supramolecular structures in the solid state, mainly due to the existence of π - π stacking interactions. Complexes 1, 2 and 4 display good catalytic activity in the homogeneous oxidation of several alkenes, cyclohexane and *n*-hexane using the "green" H_2O_2 as oxidant. This shows that polydentate N, O-donors are not a prerequisite for such activity. The difference in catalytic activity between the complexes demonstrates the importance of the substituent on the ligand to modify the ability of the oxidant or substrate to bind to the iron center for an efficient catalyst.

Work in progress in our groups includes the preparation and characterization of iron(III) complexes with other substituted benzotriazoles (including donor groups as substituents), testing their efficiency in oxidation catalysis hoping to improve selectivity, use of heterogenized iron(III)/benzotriazole catalysts and mechanistic interpretation of the results aiming at elucidation of the active oxygen species.

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Appendix A. Supplementary data

CCDC 924220, 924222, 924221 and 924223 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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Graphical Abstract



Graphical Abstract Synopsis

Reactions of benzotriazole and three of its derivatives (L) with FeCl₃ in non-polar solvents give trigonal bipyramidal [FeCl₃L₂] complexes, which display moderate to ad n high catalytic activity in the oxidation of several alkenes, cyclohexane and *n*-hexane