

Synthesis, Structure, and Catalytic Activity of New μ -Oxo-Bridged Diiron(III) Complexes

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The preparation and characterisation of two dinuclear iron(III) complexes with tripodal ligands 1,3-bis(2'-pyridylimino)isoindoline (indH) are presented. The μ -oxo-bridged diiron(III) complex $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ (**2**) has been prepared by reacting $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with indH in methanol solution. Compound $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$ (**3**) was obtained from the reaction of **2** with $\text{CH}_3\text{CO}_2\text{Ag}$ in THF. Both compounds were characterised by elemental analysis and UV/vis, IR, and Mössbauer spectroscopy. The X-ray structure analysis of $[\text{Fe}_2\text{O}(\text{ind})_2\text{Cl}_2] \cdot \text{THF}$ (**2**·THF) revealed a distorted trigonal bipyramidal ($\tau = 0.88$) coordination geometry around the

iron(III) ion. More importantly, **2** is a good functional model for the activation of small molecules as its 5-coordinate iron ions can easily coordinate such molecules. This is confirmed by the high catalase-like activity of **2**, transforming 87% of the excess of H_2O_2 into O_2 in 1 min. The complexes exhibited monooxygenase-like activity using H_2O_2 as the oxidant and oxidise alkanes to alcohols and ketones in acetonitrile in moderate yields.

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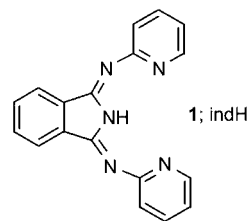
Introduction

Oxo-bridged dinuclear Fe^{III} complexes have been recently extensively studied owing to their presence in a class of non-heme iron proteins that include hemerythrin, ribonucleotide reductase, methane monooxygenase and purple acid phosphatase.^[1] The soluble methane monooxygenase, sMMO, isolated from methanotropic organisms catalyses the transformation of methane into methanol using molecular oxygen as the oxidant in the presence of a source of electrons.^[2] Several intermediates in the catalytic cycle of sMMO have been characterised but the mechanism of catalytic hydroxylation of unactivated C–H bonds is not fully understood.^[3] Spectroscopic studies implicate high-valent (μ -oxo)diiron species as intermediates in the oxidation chemistry of the diiron centres in methane monooxygenase.^[4] In the last decade several artificial sMMO systems have been developed

using μ -oxo-diiron(III) complexes derived from various supporting ligands, and oxidants such as ROOH ,^[5] H_2O_2 ,^[6] *m*-chloroperbenzoic acid,^[7] and O_2 (+ electron source).^[8] For this class of iron complexes the reactivity can be tuned by modifying the ligand around the metal centre.

Hydrogen peroxide may be the best oxidant to functionalise hydrocarbons as it is less expensive, and gives only water as a by-product. However, its use is limited, since a number of diiron complexes have catalase activity.^[9]

We report here the preparation and characterisation of μ -oxo-bridged diiron(III) complexes with the tripodal ligand 1,3-bis(2'-pyridylimino)isoindoline (**1**, indH) and their monooxygenase- and catalase-like activity.



Results and Discussion

Synthesis and Characterisation of the Complex $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$

Complex $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ (**2**) was prepared from equimolar amounts of the ligand and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. In its infrared spectrum the absorptions at 1638 and 1584 cm^{-1} indicate

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that the complex contains the deprotonated isoindoline ligand.^[10] The band at 792 cm^{-1} is characteristic of the asymmetric stretch of the Fe–O–Fe moiety, while the symmetric stretch occurs at 478 cm^{-1} .^[3a,11,12] In the electronic spectrum the band at 238 nm can be assigned to π – π^* transitions in the aromatic groups of the ligand, those in the oxo dimer region (388, 473 nm) to a weak oxo-to-iron LMCT transition. The less intense band at 473 nm is assigned to the ${}^6A_1 \rightarrow ({}^4A_1, 4E)$ transition and is the signature of the Fe–(μ -O)–Fe motif, independent of the bridging angle.^[13,14] Another important characteristic of the μ -oxo core is expected in the 550–700 nm region, which is strongly dependent on the Fe–(μ -O)–Fe angle: the lower the angle, the less energetic and/or the more intense the band.^[15] The broad, weak band at 615 nm indicates a bent structure with a low angle, in agreement with X-ray data.

Synthesis and Characterisation of the Complex $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$

Complex $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$ (**3**) was prepared by the reaction of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ with $\text{CH}_3\text{CO}_2\text{Ag}$ in THF. Infrared spectrum absorptions at 1638 and 1577 cm^{-1} indicate that the complex contains the deprotonated isoindoline ligand (absence of a strong band at 1100 cm^{-1} and absorptions in the range 1600 – 1660 cm^{-1}). Complexes with the deprotonated isoindoline ligand exhibit a weak band above 1600 cm^{-1} .^[10] The band at 752 cm^{-1} is characteristic of the asymmetric stretch of the Fe–O–Fe moiety, the symmetric stretch occurs at 510 cm^{-1} .^[3a,11,12] The $\nu(\text{CO}_2)$ bands at 1570 and 1430 cm^{-1} suggest a bridged coordination of the acetate groups. In the electronic spectrum of **3**, the band at 237 nm can be assigned to π – π^* transitions in the aromatic groups of the ligand, and bands in the oxo dimer region (385, 475 nm) assigned to an oxo-to-iron charge transfer transition. Finally a broad, weak band was observed in the low-energy visible region (720 nm). The considerable red-shift of this band, compared with λ_{max} assigned for the transition in **2**, indicates a smaller Fe–(μ -O)–Fe angle. This supports the binding mode of the acetate as a bidentate bridging ligand between the two iron atoms. From the spectroscopic data for compound **3** the $[\text{Fe}(\text{ind})(\mu\text{-O})(\mu\text{-OAc})_2(\text{ind})\text{Fe}]$ structure was proposed; however, the $[\text{Fe}(\text{ind})(\text{OAc})(\mu\text{-O})(\text{OAc})(\text{ind})\text{Fe}]$ structure could not be excluded.

Mössbauer Spectroscopy

The Mössbauer spectrum of complex $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ is shown in Figure 1 and the parameters are given in Table 1. The relatively low value of the isomer shift (IS) of **2** is due to the high population of 4s orbital of Fe^{III} and it can be explained by the s bonding between Fe^{III} and N(1) and N(6) donor atoms. The large quadrupole splitting (QS) is the consequence of the distorted trigonal bipyramidal geometry around the iron atom.^[16,17] The Mössbauer parameters of **3** represent a typical iron(III) with octahedral environment (Table 1). Namely, the higher coordination number results in a higher population of 3d orbital of iron and,

at the same time a lower s-electron density at the nucleus of Fe^{III} (higher IS) and a higher symmetry around iron atom than the trigonal bipyramidal coordination in $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$. The later effect is the origin of the smaller quadrupole splitting in the complex $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$.

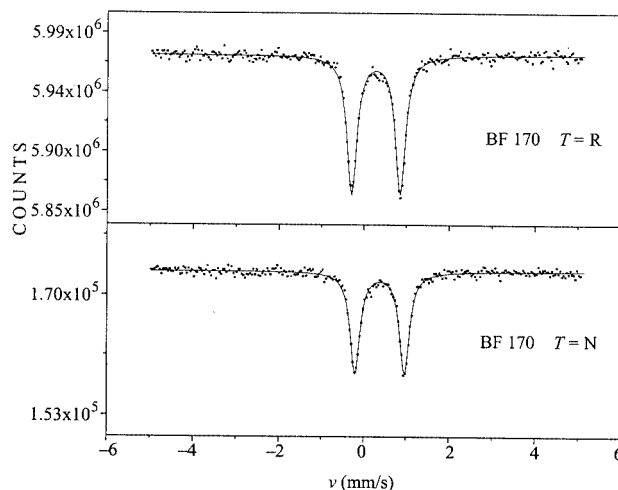


Figure 1. Mössbauer spectra of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$; T_N = temperature of liquid nitrogen

Table 1. Mössbauer parameters for complexes **2** and **3**

	$[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ $T_N^{[a]}$	room. temp.	$\text{Fe}(\text{ind})(\text{OAc})_2\text{O}$ $T_N^{[a]}$	room. temp.
IS	0.382	0.279	0.511	0.422
QS	1.164	1.143	0.645	0.617
Line width	0.274	0.284	0.318	0.360

^[a] T_N is the temperature of liquid nitrogen.

X-ray Crystal Structure of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]\cdot\text{THF}$

The molecular structure of complex $[\{\text{FeCl}(\text{ind})\}_2\text{O}]\cdot\text{THF}$ is shown in Figure 2, and selected bond lengths and angles are listed in Table 2. The complex is a μ -oxo dimer, the two iron atoms have a distorted trigonal bipyramidal geometry with $\tau = 0.88$. For perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity, respectively; τ being an index of the degree of trigonality within the structural continuum between square pyramidal and trigonal bipyramidal geometries.^[18] Oxygen and chlorine atoms and one N of the tridentate isoindolinate ligand are in basal positions, while two further N atoms of the ligand occupy apical positions. The metal–metal distance of $3.283\text{ \AA}$ is shorter than in other five-coordinated μ -oxo monobridged diiron complexes.^[12] Moreover, the Fe–O–Fe angle is significantly shorter than is usually found in similar complexes.^[5b,6a,12] These values are close to those in μ -oxo complexes with an additional bridging ligand,^[12] and also in dinuclear iron proteins.^[1a,1b,3a] The Fe–O bond lengths are within the range reported for (μ -

oxo)diiron(III) complexes^[12] and the Fe–N bond lengths are similar to those obtained for $[\text{FeCl}_2(\text{ind})]$.^[19] The Fe–N distances involving the pyridine nitrogen atoms, N1 and N3, are significantly longer than for the pyrrole nitrogen atom, N5. The same bond length pattern has been observed in Cu^{II} ^[20] and Ni^{II} ^[21] complexes of the isoindolate ligand. The Fe–Cl bond lengths are similar to those of $[\text{Fe}_2\text{O}(\text{TPA})_2\text{Cl}_2]^{2+}$.^[5b]

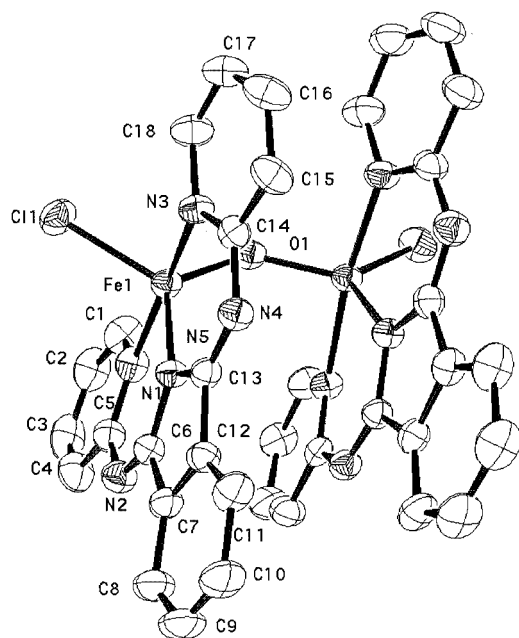


Figure 2. Molecular structure of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]\cdot\text{THF}$

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for $[\{\text{FeCl}(\text{ind})\}_2\text{O}]\cdot\text{THF}$

Fe(1)–O(1)	1.792(1)	Fe(1)–N(5)	1.998(3)
Fe(1)–Cl(1)	2.272(1)	Fe(1)–N(3)	2.161(3)
Fe(1)–N(1)	2.145(3)	N(3)–C(14)	1.360(4)
N(1)–C(5)	1.341(7)	N(5)–C(13)	1.406(5)
N(1)–C(1)	1.362(5)	N(5)–C(6)	1.384(4)
N(3)–C(18)	1.352(5)		
Fe(1)–O(1)–Fe(1)	131.9(2)	O(1)–Fe(1)–Cl(1)	116.7(1)
N(5)–Fe(1)–Cl(1)	123.4(1)	O(1)–Fe(1)–N(5)	119.8(1)
N(3)–Fe(1)–O(1)	91.2(1)	N(3)–Fe(1)–Cl(1)	92.3(1)
N(1)–Fe(1)–O(1)	96.2(1)	N(1)–Fe(1)–Cl(1)	89.0(1)
N(5)–Fe(1)–N(3)	86.3(1)	N(1)–Fe(1)–N(3)	170.8(1)
N(5)–Fe(1)–N(1)	85.3(1)		

Catalase-Like Activity

The H_2O_2 dismutation activity of complexes **2** and **3** was tested by measuring the dioxygen evolution in acetonitrile with a complex/ H_2O_2 ratio of 1:100. As expected, H_2O_2 decomposed to give O_2 gas and water, a reaction competing with the oxidation of cyclohexane. As shown in Figure 3, complex **2** exhibited rather high activity for the decomposition of hydrogen peroxide with about 80 initial turnovers per min at 25 $^\circ\text{C}$ (turnover is mmol of O_2 per mmol of complex). The yield of O_2 was 87% based on H_2O_2 after 1 min of reaction. The residual hydrogen peroxide (meas-

ured by iodometric titration) was compared with the amount of dioxygen formed and showed good agreement with the stoichiometry of the dismutation reaction. Complex **3** showed much lower dismutation activity.

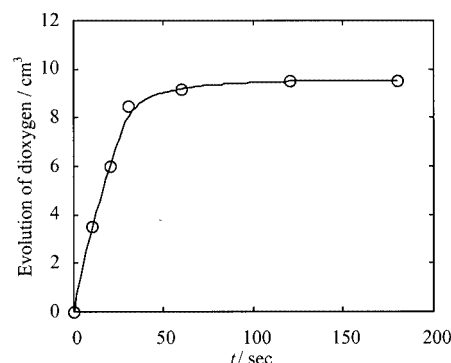


Figure 3. Evolution of dioxygen from H_2O_2 catalysed by $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$; **2** = $1.75 \text{ mol}\cdot\text{dm}^{-3}$, $[\text{H}_2\text{O}_2] = 0.175 \text{ mol}\cdot\text{dm}^{-3}$

Kinetic measurements of H_2O_2 decomposition in the presence of **2** were performed in acetonitrile at 25 $^\circ\text{C}$ under pseudo-first-order conditions. To determine the rate dependence on the two reactants, runs were performed at various $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ and H_2O_2 concentrations. The straight line obtained by plotting the initial reaction rate against the initial catalyst concentration indicates a reaction order of one with respect to **2**. The first-order dependence of the reaction rate against $[\text{H}_2\text{O}_2]$ was established by plotting the initial reaction rate against the $[\text{H}_2\text{O}_2]$. On the basis of the kinetic data the rate law (1) could be derived. The second-order rate constant k was found to be $9.2 \pm 0.6 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{s}^{-1}$.

$$\text{Reaction rate} = k[\text{H}_2\text{O}_2][\text{2}] \quad (1)$$

UV/vis spectra of a solution of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ recorded immediately after addition of the oxidant show drastic changes (Figure 4). The final spectrum is very similar to that obtained in the reaction of some other (μ -oxo)diiron(III) complexes with H_2O_2 .^[6b] This may indicate that in the reaction with hydrogen peroxide the original bent μ -oxo structure decomposes to form a linear μ -oxo type or a mononuclear complex.

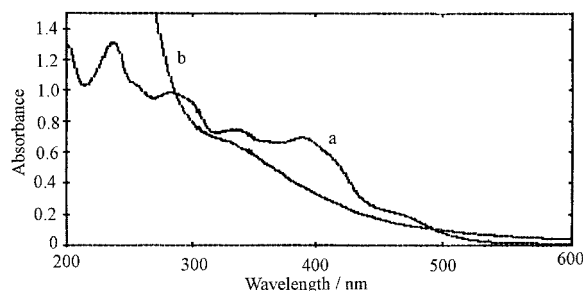


Figure 4. UV/vis spectra of (a) $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$, (b) **2** with 100 equiv. of H_2O_2 added. **2** = $4.02 \cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$, CH_3CN , 25 $^\circ\text{C}$

Table 3. Oxidation of cyclohexane

Catalyst ^[a]	Oxidant	Yield [%] ^[b]			TN ^[c] ^[d]
		Cyclohexanol	Cyclohexanone	<i>t</i> BuO ₂ /cyclohexane	
[{FeCl(ind)} ₂ O]	H ₂ O ₂	14.6	14.8	—	29.4
[{FeCl(ind)} ₂ O]	H ₂ O ₂	15.3	13.8	—	29.1 ^[d]
[{FeCl(ind)} ₂ O]	H ₂ O ₂	12.2	13.6	—	25.8 ^[e]
[{Fe(ind)(OAc)} ₂ O]	H ₂ O ₂	4.5	8.4	—	12.9
[FeCl ₂ (ind)]	H ₂ O ₂	4.3	6.6	—	10.9
[{FeCl(ind)} ₂ O]	<i>t</i> BuO ₂ H	7.2	7.2	0.5	14.9
[{Fe(ind)(OAc)} ₂ O]	<i>t</i> BuO ₂ H	7.2	7.4	0.6	15.2

^[a] Reaction conditions: cyclohexane (3.5 mmol), oxidant (3.5 mmol), catalyst (35 μ mol), acetonitrile (10 cm³), Ar, 25 °C, 10 h. ^[b] Based on the oxidant. ^[c] TN (turnover numbers) = mol of product per mol of catalyst. Total yield and TN values take into account that 2 equivalents of oxidant are required to make 1 equivalent of ketone. ^[d] Under O₂. ^[e] 1 cm³ CCl₄ added.

Oxygenation of Alkanes

The monooxygenase-like activity of complexes [{FeCl(ind)}₂O] (**2**), [{Fe(ind)(OAc)}₂O] (**3**) and [FeCl₂(ind)] was tested in the oxidation of alkanes. We checked first the activity of (**2**) in the oxidation of cyclohexane by different oxidants and in different solvents (MeOH, CH₂Cl₂, CH₃CN). Catalytic oxidations were effective only with H₂O₂ and *t*BuO₂H. No oxidation products could be detected with di-*tert*-butyl peroxide and iodosylbenzene. The results (Table 3) show that the best yields were obtained with H₂O₂ in acetonitrile. Under our experimental conditions the molar ratio of iron complex/hydrogen peroxide/substrate is 1:100:100. The oxidation of cyclohexane yielded cyclohexanol and cyclohexanone in a 2:1 ratio. The total turnover number (mmol product per mmol catalyst) was 29.4, and the alcohol + ketone yield was 29.4% after 10 h. In comparison, the yield was 14.9% with *t*BuO₂H and a small amount of *tert*-butyl cyclohexyl peroxide was also formed. Moreover, the catalyst obtained by replacing the chlorine ligands with acetate was less active. The mononuclear iron(III) complex, [FeCl₂(ind)], showed a catalytic activity similar to that of **2**.

As shown in Table 4, complex **2** also catalyses the oxygenation of methylcyclohexane, adamantane, and ethylbenzene. With methylcyclohexane as substrate, the reactivity at the tertiary position is 6 times higher than that at the secondary position, and no oxygenation was observed at the primary position. The normalised reactivity ratio of the tertiary C–H to secondary C–H in the oxygenation of adamantane is 4.0. The adamantane C3/C2 selectivity ratio is in the range found for other systems, including model studies of sMMO by using dinuclear iron complexes,^[5a] and also for the MMO enzyme (3.0, normalised).^[22] These results show that the regio-selectivity in the alkane hydroxylation catalysed by [{FeCl(ind)}₂O] follows the order tertiary > secondary > primary carbon. From the time dependence of the reaction (Figure 5) it seems that cyclohexanol and cyclohexanone were always formed in approximately constant ratios, showing that cyclohexanol is not the precursor of cyclohexanone. Experiments were also performed under dioxygen to elucidate the role of O₂. The almost constant yields of the oxidation products, whether the reaction was carried out under argon or dioxygen, suggest that O₂ is not involved in

this reaction (Table 2). When 2,6-di-*tert*-butyl-4-methylphenol, as a free radical trap, was added to the oxidation of cyclohexane prior to H₂O₂ addition in the case of complex **2** there was no significant lowering of the yields of oxidation products. The oxidation reaction of cyclohexane was also performed after addition of CCl₄ to the reaction mixture. No formation of bicyclohexyl and cyclohexyl chloride was observed. Any free cyclohexyl radical present would undergo dimerisation to give bicyclohexyl, and would also abstract Cl from CCl₄ to give cyclohexyl chloride.^[23]

Table 4. Oxygenation of alkanes catalysed by [{FeCl(ind)}₂O]

Substrate ^[a]	Product	Yield [%] ^[b]	TN ^[c]
Methylcyclohexane	1-methylcyclohexanol	4.2	15.4
	2-methylcyclohexanol	0.4	
	3-methylcyclohexanol	1.8	
	3-methylcyclohexanone	6.2	
	4-methylcyclohexanone	2.8	
Adamantane ^[d]	1-adamantanol	9.2	16.7
	2-adamantanol	6.3	
	adamantanone	1.2	
Ethylbenzene	1-phenylethanol	2.5	16.1
	acetophenone	13.6	

^[a] Reaction conditions: substrate (3.5 mmol), oxidant (3.5 mmol), **2** (35 μ mol), acetonitrile (10 cm³), Ar, 25 °C, 10 h. ^[b] Based on the oxidant. ^[c] TN (turnover numbers) = mol of product per mol of catalyst. Total yield and TN values take into account that 2 equiv. of oxidant are required to make 1 equiv. of ketone. ^[d] 20 cm³ acetonitrile.

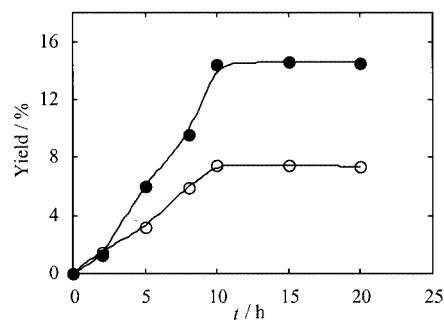


Figure 5. Yields of the products versus reaction time for the oxygenation of cyclohexane, catalyst [{FeCl(ind)}₂O]; (•) cyclohexanol, (○) cyclohexanone; [cyclohexane] = 0.35 mol·dm⁻³, [H₂O₂] = 0.35 mol·dm⁻³, [**2**] = 3.5 · 10⁻³ mol·dm⁻³, CH₃CN 10 cm³, Ar, 25 °C

In our study the coordinatively unsaturated iron(III) in $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ can easily bind H_2O_2 , and an iron-peroxo species, observed also during other H_2O_2 dependent reactions,^[24–26] may be a transient precursor of a metal-based oxidative species. Our observations suggest that the reaction proceeds via heterolytic scission of the peroxide bond, resulting in high-valent oxo metal intermediates, rather than via a radical mechanism. The same reaction also occurs with $[\text{FeCl}_2(\text{ind})]$. It is likely that the mononuclear $[\text{FeCl}_2(\text{ind})]$ in solution is converted into the oxo-bridged dimer (**2**), the thermodynamic sink for the Fe^{III} state, and this will be the active catalyst of the reaction. Compound **2** could also be prepared by stirring $[\text{FeCl}_2(\text{ind})]$ in hot methanol. In $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$, obtained by replacing chlorine ligands by acetate bridges, the six-coordinated iron(III) has no vacant site for the coordination of H_2O_2 , which results in lower activity. Further spectroscopic studies are needed to elucidate the structure of the intermediate complexes.

Conclusion

Two new μ -oxo-diiron(III) complexes with 1,3-bis(2'-pyridylimino)isoindoline ligands, $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ (**2**), $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$ (**3**), have been prepared and then characterised by elemental analysis and UV/vis, IR, and Mössbauer spectroscopy. X-ray structure analysis of the complex $[\text{Fe}_2\text{O}(\text{ind})_2\text{Cl}_2]\cdot\text{THF}$ revealed that the coordination geometry around the iron(III) ion is distorted trigonal bipyramidal ($\tau = 0.88$). In complex **3** the iron(III) has an octahedral environment. Moreover **2** is a good functional model for the activation of small molecules, since each iron ion is five-coordinate and, thus, small substrate molecules can be coordinated easily. Both complexes were effective catalysts for the oxidation of alkanes utilising hydrogen peroxide as oxygen source; however, their use is limited due to their ability to dismutate H_2O_2 . Complex **2** exhibits a rather high activity for the decomposition of hydrogen peroxide, transforming 87% of the excess of H_2O_2 into O_2 in 1 min.

Experimental Section

General Remarks: All manipulations were performed under a pure dinitrogen or argon atmosphere unless otherwise stated, using standard Schlenck-type inert-gas techniques.^[27] 1,3-Bis(2'-pyridylimino)isoindoline,^[28] and $[\text{FeCl}_2(\text{ind})]$ ^[19] were prepared according to literature methods. Methanol and acetonitrile were purified in the usual manner and stored under argon.^[29] All other chemicals were commercial products and were used as received without further purification.

Physical Measurements: Infrared spectra were recorded on a Specord 75 IR (Carl Zeiss) spectrophotometer using samples mullied in Nujol between KBr plates or in KBr pellets. GC analyses were performed on a HP 5830A gas chromatograph equipped with a flame ionisation detector and a 25 m (0.2 mm i.d., 0.25 μm FT) CP-SIL-8CB fused silica capillary column. GC-MS analyses were performed on a HP 5890II/5971 GC/MSD apparatus equipped

with a column identical to that used for GC analyses. UV/vis spectra were recorded on a Shimadzu UV-160 spectrophotometer by using quartz cells. The Mössbauer spectroscopy measurements were carried out at room temp. or at liquid nitrogen temperature (T_{N}) and in zero applied magnetic field using a conventional Mössbauer spectrometer in constant acceleration mode. The γ -rays were provided by a $^{57}\text{Co}(\text{Rh})$ source of 10^9 Bq activity. All isomer shift data are given relative to α -Fe. For the spectrum evaluation we used the MössWinn program package.^[30]

Synthesis of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ (2**):** $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (0.270 g, 1 mmol) was dissolved in methanol (10 cm^3), then 1,3-bis(2'-pyridylimino)isoindoline (0.299 g, 1 mmol) in methanol (20 cm^3) was added and the reaction mixture stirred under argon at 60° for 8 h. After cooling, a dark brown powder of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ precipitated, which was filtered off, washed with acetonitrile and dried under vacuum (0.34 g, 85%). Recrystallisation of the product from THF gave dark brown crystals. M.p. $354\text{--}356^\circ\text{C}$. IR (KBr): $\tilde{\nu} = 1638$ w, 1602 w, 1584 s, 1549 m, 1536 s, 1468 s, 1428 m, 1360 w, 1306 w, 1265 m, 1197 m, 1150 w, 1095 w, 1061 s, 1007 m, 898 w, 851 w, 792 m, 783 s, 722 m, 702 m, 641 w, 539 w, 514 w, 478 w, 437 cm^{-1} . UV/vis (CH_3CN): λ_{max} ($\log \epsilon/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 238 (4.78), 282 (4.65), 388 (4.51), 473 (3.99), 615 (3.57) nm. $\text{C}_{36}\text{H}_{24}\text{Cl}_2\text{Fe}_2\text{N}_{10}\text{O}$ (795.2): calcd. C 54.36, H 3.04, Cl 8.91, Fe 14.04, N 17.61; found C 54.68, H 3.12, Cl 8.54, Fe 13.44, N 17.34.

Synthesis of $[\{\text{Fe}(\text{ind})(\text{OAc})\}_2\text{O}]$ (3**):** $[\{\text{FeCl}(\text{ind})\}_2\text{O}]$ (1.067 g, 1.34 mmol) in THF (80 cm^3) was treated with $\text{CH}_3\text{CO}_2\text{Ag}$ (0.447 g, 2.68 mmol) at 60°C for 8 h. The resultant light brown precipitate was filtered off and the solution condensed under vacuum to 30 cm^3 . Upon cooling (-10°C), a dark brown solid was deposited, which was filtered off, washed with acetonitrile and dried under vacuum (0.75 g, 65%). M.p. $> 320^\circ\text{C}$. IR (KBr): $\tilde{\nu} = 1638$ w, 1597 w, 1577 s, 1570 s, 1530 s, 1468 s, 1430 s, 1367 w, 1272 m, 1190 m, 1150 w, 1061 s, 1000 m, 878 w, 802 m, 797 s, 752 m, 539 w, 510 w, 430 cm^{-1} . UV/vis (THF): λ_{max} ($\log \epsilon/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 237 (4.51), 363 (4.32), 385 (4.35), 409 (4.28), 475 (3.84) 720 (2.45) nm. $\text{C}_{40}\text{H}_{30}\text{Fe}_2\text{N}_{10}\text{O}_5$ (842.4): calcd. C 57.02, H 3.58, Fe 13.25, N 16.63; found C 56.74, H 3.60, Fe 12.97, N 16.57.

Table 5. Crystallographic data of $[\{\text{FeCl}(\text{ind})\}_2\text{O}]\cdot\text{THF}$

Empirical formula	$\text{C}_{36}\text{H}_{24}\text{N}_{10}\text{OFe}_2\text{Cl}_2\cdot\text{THF}$
Formula mass	867.36
Crystal size [mm^3]	$0.7 \times 0.2 \times 0.1$
Crystal system	orthorhombic
Space group	Pccn
a [$\text{\AA}$], α [$^\circ$]	12.727(1), 90
b [$\text{\AA}$], β [$^\circ$]	13.460(1), 90
c [$\text{\AA}$], γ [$^\circ$]	21.516(1), 90
V [$\text{\AA}^3$]	3685.8(4)
Z	4
$F(000)$	1840
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.621
μ [mm^{-1}]	0.992
$\Theta_{\text{min.}}, \Theta_{\text{max.}}$ [$^\circ$]	2.90, 26.36
Reflections collected	4014
Reflections total	3632
Reflections unique	2243
Parameters	254
GOF on F^2	1.027
R [$I \geq 2\sigma(I)$] (all data)	0.0502 (0.1028)
R_w (all data)	0.1047 (0.1253)
Max. resd. density [$\text{e/\AA}^3$]	0.577

X-ray Structure Determination of 2: Suitable crystals of $[\{\text{FeCl}(\text{ind})_2\text{O}\} \cdot \text{THF}]$ were obtained from THF. The intensity data were collected with a Nonius Kappa CCD single-crystal diffractometer, using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and ϕ scan technique at 293 K. Details of the crystal structure determination are shown in Table 5. The structure was solved by direct and difmap methods (SIR92),^[31] and refined on F^2 by using full-matrix least-squares methods.^[32,33] CCDC-195083 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

Oxidation Reactions: Standard oxidation reactions were carried out under an inert atmosphere of argon. The complex (35 μmol) was dissolved in acetonitrile (10 cm^3) containing 3.5 mmol of substrate. The reaction was then started by adding 3.5 mmol of H_2O_2 or $t\text{BuO}_2\text{H}$. After stirring for 10 h at 25 °C the products were determined by GC analysis. The structures of the products were confirmed by GC-MS spectrometry, and by comparison with authentic samples.

Catalase-Like Reactions: All reactions were carried out at 25 °C under an argon atmosphere in a thermostatted reactor with stirring. To start the reaction hydrogen peroxide (0.875 mmol, 97 μL) was added through a septum to a stirred solution of the complex (8.75 mmol, 7 mg) in acetonitrile (5 cm^3). The volume of evolved dioxygen was read periodically by using a gas burette. In the kinetic measurements the hydrogen peroxide concentration was first kept constant ($[\text{H}_2\text{O}_2] = 0.175 \text{ mol} \cdot \text{dm}^{-3}$) and the concentration of **2** was varied from 0.525 to 3.52 $\text{mol} \cdot \text{dm}^{-3}$. To determine the rate dependence on the H_2O_2 , the catalyst concentration was kept constant ($[\text{2}] = 1.75 \text{ mol} \cdot \text{dm}^{-3}$) and the $[\text{H}_2\text{O}_2]$ varied in the range 0.0618–0.3088 $\text{mol} \cdot \text{dm}^{-3}$.

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