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Chemical origin of high activity in oxygenation of cyclohexane by H_2O_2 catalysed by dinuclear iron(III) complexes with amide-containing ligands†

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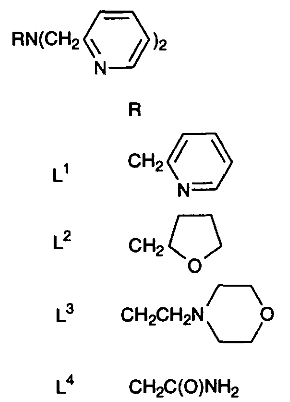
The crystal structures of two dinuclear iron(III) complexes containing an oxo bridge, $[Fe_2OCl_2L_2][ClO_4]_2{\cdot}2H_2O$ **1** [L = *N,N*-bis(2-pyridylmethyl)glycinamide] and $[Fe_2OCl_2L_2][ClO_4]_2$ **2** (L = *N*-{2-[bis(2-pyridylmethyl)amino]ethyl}morpholine) were determined. Their structural features are quite similar to those of the corresponding linear dinuclear complex $[Fe_2OCl_2(tpa)_2][ClO_4]_2$, where tpa is tris(2-pyridylmethyl)amine; the ligands act as tetradentate tripods, and the Fe–O (amide) and average Fe–N (morpholine) distances are 2.165(6) and 2.45(1) Å, respectively. Complex **1** exhibited much higher activity for the hydroxylation of cyclohexane in the presence of H_2O_2, while the activities of the other two complexes are negligible. In contrast, all three complexes exhibited high activity for the decomposition of H_2O_2. These results indicate that the active species for oxygenation of cyclohexane, which may be an iron(III)–peroxide adduct (**I**), should be different from that for decomposition of H_2O_2, adduct **II**, and that these two species may exist in the solution of complex **1**. It is postulated that adduct **I** may be a dinuclear iron(III)–η^1-hydroperoxide species stabilized through hydrogen bonding between the hydroperoxide ion and the oxygen atom of the amide group. Extended-Hückel molecular orbital calculations showed that the hydrogen bonding may lead to induction of high 'oxo-like' activity in the peroxide adduct. In the cases of the tpa and morpholine complexes the formation of a η^1-hydroperoxide adduct seems unfavourable because of both steric and electronic reasons; instead a (μ-η^1:η^1-peroxo)diiron(III) species, adduct **II**, is formed which induces high catalase-like activity.

In the last decade a number of μ-oxo-diiron(III) complexes have been synthesized which model well the structural and spectroscopic properties of the metal sites in diiron–oxo proteins,[1] but few of these species display catalytic activity which mimics the alkane functionalization chemistry of methane monooxygenase.[2] Que and co-workers[3] have found that iron(III) complexes of tris(2-pyridylmethyl)amine (L^1) serve as remarkable functional models, mimicking the oxidation reactions catalysed by non-haem iron enzymes. They also reported that a dinuclear iron(III) complex with a μ-oxo bridge, $[Fe_2OL^1{}_2][ClO_4]_4$, affords a high-valent oxo-iron species upon reaction with hydrogen peroxide, and proposed that it is an intrinsically active species for alkane hydroxylation.[4]

In a previous paper[5] we reported that a dinuclear linear μ-oxo diiron(III) complex, $[Fe_2OCl_2L^2{}_2]^{2+}$, exhibited high activity for oxygenation of cyclohexane in the presence of hydrogen peroxide, while the corresponding activities of the corresponding compounds of L^1 and L^3 are almost negligible. Since the iron(III) complex with L^2 shows negligible activity for the decomposition of hydrogen peroxide in spite of the very high catalase-like function of the L^1 and L^3 complexes, we have concluded that there are two different kinds of peroxide adducts in solution; one is active for oxygenation of cyclohexane, and another has catalase-like activity.[6] According to studies on the catalase-like activity of dinuclear iron(III) compounds, it has been assumed that an active species may be a (μ-η^1:η^1-peroxo)diiron(III) species (see Scheme 1).[7–10] As an active species for oxygenation of cyclohexane, we have assumed formation of a dinuclear iron(III)–peroxide adduct with η^1 co-ordination (see adduct **III** in Scheme 1), where the peroxide ion interacts with a tetrahydrofuran ring.[5]

Very recently we have observed that a dinuclear iron(III) complex with a tripodal ligand containing an amide group, L^4, exhibits high activity for both oxygenation of cyclohexane and decomposition of hydrogen peroxide. In this article the experimental details of the preparation and crystal structure determination of this compound are given and the origin of its high activity, will be revealed based on the results of extended-Hückel molecular orbital (EHMO) calculations.



Experimental

Materials

The compounds L^4 and L^3 were obtained from pyridine-2-carbonyl chloride and the amine [glycinamide and *N*-(2-aminoethyl)morpholine] according to the methods reported by Toftlund and Andersen.[11] By use of a methanol solution of L^3 or L^4, iron(III) chloride hexahydrate, a stoichiometric amount of triethylamine,[1c] and sodium perchlorate, the desired complexes, $[Fe_2OCl_2L^4{}_2][ClO_4]_2{\cdot}2H_2O$ **1** (yield: 20%) and $[Fe_2OCl_2L^3{}_2][ClO_4]_2$ **2** (yield: 15%) were obtained as orange crystals (Found: C, 36.6; H, 3.65; N, 11.95. Calc.: C, 36.25; H, 3.7; N, 11.95. Found: C, 41.75; H, 4.8; N, 10.7. Calc.: C 42.3; H, 4.75; N, 10.95%).

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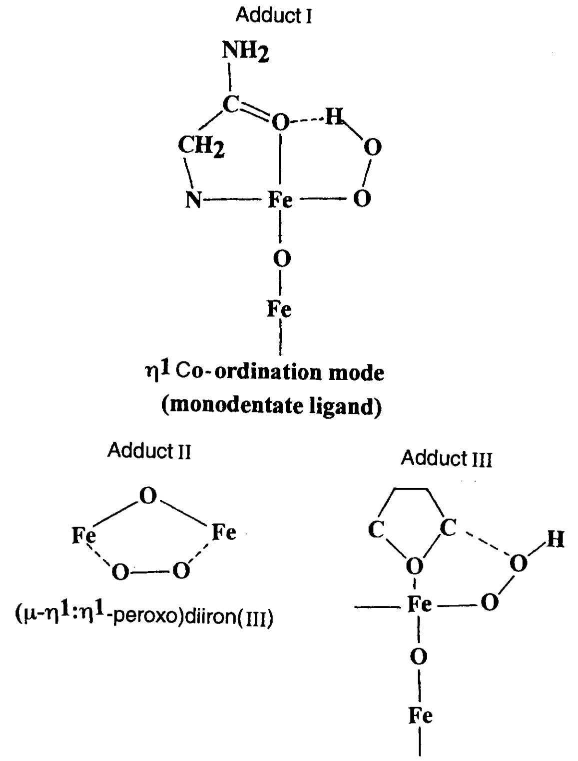
† *Non-SI unit employed:* eV ≈ 1.60 × 18^{-19} J.



Scheme 1

Crystallography

Crystals of complexes **1** and **2** were mounted on a glass fibre. All measurements were made on a Rigaku 5S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at 296 K and a 12 kV rotating-anode generator at Saga University. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angle of 25 carefully centred reflections. The cell constants and the crystal data are summarized in Table 1. The data were corrected for Lorentz-polarization effects. The structures were solved by the direct method, and non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Weber.[12] Anomalous dispersion factors were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. All the calculations were performed using the TEXSAN crystallographic software package.[13]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/235.

Catalase-like activity of complexes

All reactions were performed at 20 °C in a reactor (10 cm^3) containing a stirring bar under air. The flask containing an iron(III) complex (10 μmol) solution (5 cm^3 acetonitrile) was closed with a rubber septum. Hydrogen peroxide solution (1 cm^3, commercial 30% aqueous solution diluted to 1 mol dm^{-3} in acetonitrile) was injected through the septum with a syringe. The reactor was connected to a graduated burette filled with water and the dioxygen evolved was measured at appropriate times by volumetry.

Oxygenation of cyclohexane

In a typical run an acetonitrile solution (20 cm^3) containing iron(III) complex (0.05 mmol) and cyclohexane (840 mg) was added to an acetonitrile solution (10 cm^3) containing hydrogen peroxide (1.13 g of commercial 30% aqueous solution), and allowed to stand for 6 h at room temperature. After 2 h the products were determined by GC. Cyclopentanone was used as an internal standard. The experiments were also done at 0 °C.

Molecular orbital calculations

Molecular orbital calculations for $[Fe(NH_3)_4(HCONH_2)(HO_2)]^{2+}$ and $[Fe(NH_3)_5(O_2)]^+$ were performed by the use of the EHMO method reported by Hoffmann;[14] the parameters used for the iron(III) ion are the same as those in the literature,[15] and the positional parameters of formamide were determined by the use of a crystal structure determination.

Results and Discussion

Crystal structure

The ORTEP[16] representations of the cations of compounds **1** and **2** are shown in Figs. 1 and 2, and selected bond lengths and angles are listed in Table 2. The L^4 complex **1** is μ-oxo dimer with a linear Fe–O–Fe structure, which is required by the centre of symmetry at the bridging oxygen atom. An almost linear structure with a μ-oxo bridge is found for the L^3 complex **2**; Fe–O–Fe angle 176.0(5)°. The Fe–μ-O bond distances are in the range 1.780–1.800 Å, within that reported for μ-oxo-diiron(III) complexes.[1a] The Fe–N (pyridine), average 2.13–2.14 Å, and Fe–N (amine), average 2.22 Å, distances are also typical for the analogous L^1 compounds.[3] It should be noted here that the Fe–O (amide oxygen atom, located *trans* to the μ-oxo oxygen) distance in **1** is 2.165(6) Å, which is shorter than that of Fe–N (pyridine) 2.263(6) Å in the corresponding L^1 complex.[3] These data indicate that the co-ordination ability of an amide oxygen atom toward iron(III) is rather strong. The average Fe–N (amine of morpholine ring) distance in the L^3 complex is 2.45(1) Å. The chloride ligands co-ordinate *trans* to the amine nitrogen on each iron centre and *anti* to each other relative to the Fe–O–Fe axis. The Fe–Cl bond lengths are comparable to those reported previously.[3]

Oxygenation of cyclohexane

In Table 3 the turnover numbers of the products, cyclohexanol and cyclohexanone, are listed; it should be noted here that the dinuclear iron(III) complex with L^4 exhibits much higher activity for the oxygenation of cyclohexane, while those of L^1 and L^3 exhibited negligible activity under the same experimental conditions. The time courses of the product formation at 0 °C are illustrated in Fig. 3; the results are consistent with those in Table 3.

Active species for decomposition of hydrogen peroxide

The H_2O_2 dismutation activity was tested by measuring the dioxygen evolution over 60 min in acetonitrile with a complex: H_2O_2 ratio of 1:100. As shown in Fig. 4, the three iron(III) compounds used exhibited rather high activity for decomposition of hydrogen peroxide. These results on the oxygenation of cyclohexane and catalase-like activity clearly demonstrate that there are two different kinds of iron(III)–peroxide adduct in solution, and that the structure of the active species for decomposition of hydrogen peroxide is different from that for the oxygenation of cyclohexane. Previously we investigated the catalase-like activity of dinuclear iron(III) compounds with a μ-alkoxo bridge, and concluded that the active species for decomposition of hydrogen peroxide has a dimeric (μ-η^1:η^1-peroxo)diiron(III) structure;[7] this conclusion was supported by other work.[6–9] According to recent studies[17] it is clear that structure of μ-oxo dinuclear iron(III) complexes is rather flexible

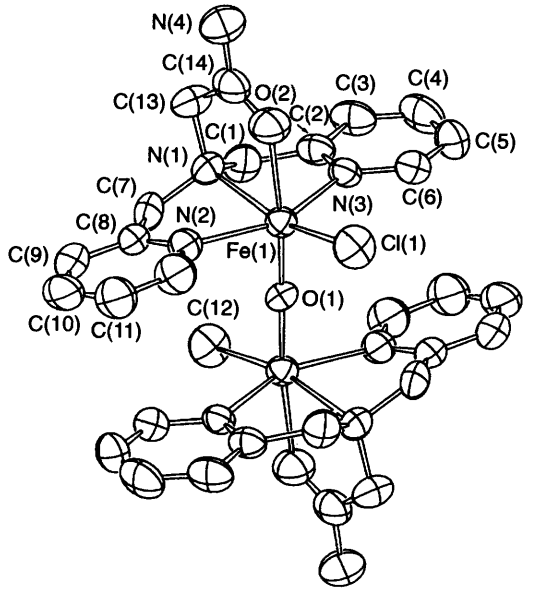


Fig. 1 An ORTEP drawing of $[Fe_2OCl_2L^4{}_2]^{2+}$ (ellipsoids at the 50% probability level)

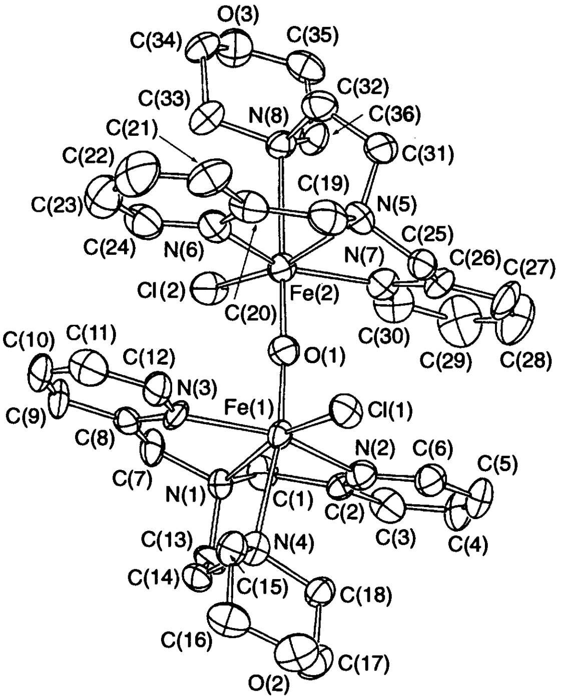


Fig. 2 An ORTEP drawing of $[Fe_2OCl_2L^3{}_2]^{2+}$ (ellipsoids at the 50% probability level)

in solutions containing water or hydrogen peroxide, providing support for the linear iron(III) complex with L^1 assuming a bent peroxide adduct facilely, as shown below. This will explain the high catalase-like activity of the linear L^1 complex observed in this study, and is quite consistent with our recent observation that the dinuclear complex $[Fe_2O(O_2CMe)L^1{}_2]^{3+}$ with bent structure also exhibits high catalase-like activity.[18] The same reasoning may be applied to the L^3 and L^4 complexes, since they exhibit high catalase-like activity.

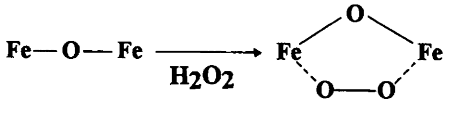


Table 1 Crystallographic data* for complexes 1 and 2

	1	2
Formula	$C_{28}H_{36}Cl_4Fe_2N_8O_{13}$	$C_{36}H_{48}Cl_4Fe_2N_8O_{11}$
M	946.15	1022.34
Crystal dimensions/mm	0.3 × 0.2 × 0.35	0.4 × 0.4 × 0.5
Crystal symmetry	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.65(1)	12.71(2)
b/Å	12.813(4)	15.799(2)
c/Å	7.882(1)	21.930(3)
α/°	106.94(2)	
β/°	93.88(5)	95.40(5)
γ/°	106.99(5)	
U/Å^3	970(1)	4385(6)
Z	1	4
D_c/g cm^3	1.619	1.546
$F(000)$	484	2112
μ(Mo-Kα)/cm^{-1}	10.93	9.70
Transmission factors	0.93–1.00	0.91–1.00
Data collected	4698	8426
Observed data [$I > 3\sigma(I)$]	2144	3308
No. variables	250	550
$R(R')$	0.061(0.069)	0.063(0.077)
Goodness of fit	1.73	1.99
Final ΔF residual/e Å^{-3}	0.72	1.08

* Details in common: scan type ω–2θ; $w = 4F_o{}^2/\sigma^2(F_o)^2$; function minimized $\Sigma w(|F_o| - |F_c|)^2$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$.

Table 2 Selected bond distances (Å) and angles (°)

Complex **1** (centrosymmetric)			
Fe(1)–Cl(1)	2.276(2)	Fe(1)–O(1)	1.780(2)
Fe(1)–O(2)	2.165(6)	Fe(1)–N(1)	2.245(5)
Fe(1)–N(2)	2.136(6)	Fe(1)–N(3)	2.123(5)
Cl(1)–Fe(1)–O(1)	101.96(8)	Cl(1)–Fe(1)–O(2)	86.2(2)
Cl(1)–Fe(1)–N(1)	163.9(2)	Cl(1)–Fe(1)–N(3)	101.8(2)
Cl(1)–Fe(1)–N(2)	103.9(2)	O(1)–Fe(1)–O(2)	171.8(2)
O(1)–Fe(1)–N(1)	95.0(2)	O(1)–Fe(1)–N(2)	91.2(2)
O(1)–Fe(1)–N(3)	92.3(2)	O(2)–Fe(1)–N(1)	76.8(2)
O(2)–Fe(1)–N(2)	86.4(2)	O(2)–Fe(1)–N(3)	86.3(2)
N(1)–Fe(1)–N(2)	75.6(2)	N(1)–Fe(1)–N(3)	77.1(2)
N(2)–Fe(1)–N(3)	152.6(2)		
Complex **2**			
Fe(1)–O(1)	1.794(8)	Fe(2)–O(1)	1.800(8)
Fe(1)–N(2)	2.15(1)	Fe(2)–Cl(2)	2.289(4)
Fe(1)–Cl(1)	2.307(4)	Fe(2)–N(5)	2.19(1)
Fe(1)–N(1)	2.20(1)	Fe(2)–N(6)	2.14(1)
Fe(1)–N(3)	2.110(9)	Fe(2)–N(7)	2.15(1)
Fe(1)–N(4)	2.43(1)	Fe(2)–N(8)	2.47(1)
Fe(1)–O(1)–Fe(2)	176.0(5)	Cl(2)–Fe(2)–O(1)	102.5(3)
Cl(1)–Fe(1)–O(1)	100.9(3)	Cl(2)–Fe(2)–N(5)	161.8(3)
Cl(1)–Fe(1)–N(1)	165.4(3)	Cl(2)–Fe(2)–N(6)	104.9(3)
Cl(1)–Fe(1)–N(2)	100.8(3)	Cl(2)–Fe(2)–N(7)	99.3(3)
Cl(1)–Fe(1)–N(3)	103.1(3)	O(1)–Fe(2)–N(5)	95.2(3)
O(1)–Fe(1)–N(1)	93.4(4)	O(1)–Fe(2)–N(6)	91.3(4)
O(1)–Fe(1)–N(2)	90.6(4)	O(1)–Fe(2)–N(7)	92.6(4)
O(1)–Fe(1)–N(3)	91.1(4)	N(5)–Fe(2)–N(6)	78.8(4)
N(1)–Fe(1)–N(2)	76.1(4)	N(5)–Fe(2)–N(7)	75.4(4)
N(1)–Fe(1)–N(3)	79.2(4)	N(6)–Fe(2)–N(7)	154.1(4)
N(2)–Fe(1)–N(3)	155.3(4)		

As described above, it seems reasonable to consider that the active species for oxygenation of cyclohexane should be different from that for the catalase-like reaction, and that the former should be inactive for decomposition of hydrogen peroxide; this suggests that there may be another peroxide adduct in the solution of hydrogen peroxide and the L^4 complex. Many dinuclear iron(III) peroxides are assumed to clarify the chemical mechanism of dioxygen activation in methane monooxygenase.[19] Fontecave and co-workers[8] have considered an oxoiron-(V) or -(IV) species for hydroxylation of cyclohexane. We have postulated an iron(III)-hydroperoxide adduct with η^1 co-ordination (see adduct **III** in Scheme 1),[5,20,21] and reported that these adducts are inactive for the oxidation reaction.[21] Thus, in this study we have performed theoretical calculations on the η^1-hydroperoxide adduct **I**; in this adduct, the oxygen atom of the hydroperoxide ion is assumed to be hydrogen bonded with the oxygen atom of the amide group, and such adduct formation is less favourable for the L^1 and L^3 analogues.

Molecular orbital calculations and activation of peroxide ion

In Fig. 5 some of the results of calculations on $[Fe(NH_3)_5(O_2)]^+$ performed by the EHMO method are shown. It should be noted here that the $d_{x^2-y^2}$ orbital, which interacts with the peroxide ion, contains considerable contributions from p_x and p_z orbitals of atom O(1) and also the p_z orbital of O(2). Since this orbital is half filled it can interact with the occupied orbital of the organic substrate at O(1) or O(2) as indicated by the arrow in Fig. 5. We will call case (1) that where the metal–peroxide adduct acts as like an oxometal compound, *i.e.* oxo-like reactivity,[20] and case (2) that experimentally confirmed previously, *i.e.* where the benzene ring neighbouring the iron(III) ion was facilely hydroxylated to yield phenol in the presence of hydrogen peroxide.[21]

The results of EHMO calculations performed on $[Fe(NH_3)_4(HCONH_2)(HO_2)]^{2+}$ as a model compound for adduct **I** are illustrated in Fig. 6. Orbital 5, which consists of the metal $d_{x^2-y^2}$ orbital and p orbitals of the peroxide ion is very similar to that in $[Fe(NH_3)_5(O_2)]^+$. It should be noted that in adduct **I** there are several orbitals which have contributions from the oxygen atom of the amide group and the peroxide ion co-ordinated to iron(III). The presence of orbitals B and C in Fig. 6 suggests that some electronic interaction between the oxygen atoms of the peroxide ion [O(2)] and the amide group occurs *via* a half-filled d orbital, and this interaction should contribute to the stabilization of the

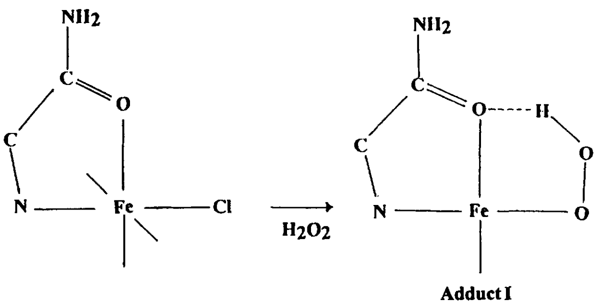


Table 3 Turnover numbers of the products after 2 h

Complex	Cyclohexanol	Cyclohexanone
L^4	4.0	3.2
L^3	0.8	0.8
L^1	0.3	0.3

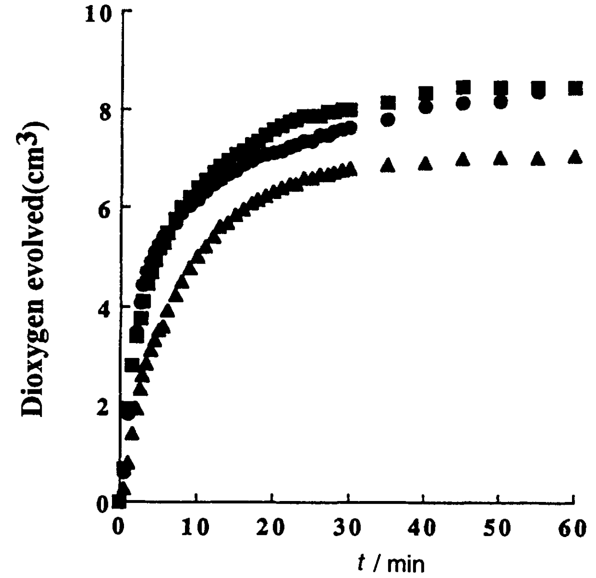


Fig. 4 Evolution of dioxygen catalysed by the iron(III) complexes in the presence of hydrogen peroxide (25 °C): ■, L^3; ●, L^1; ▲, L^4

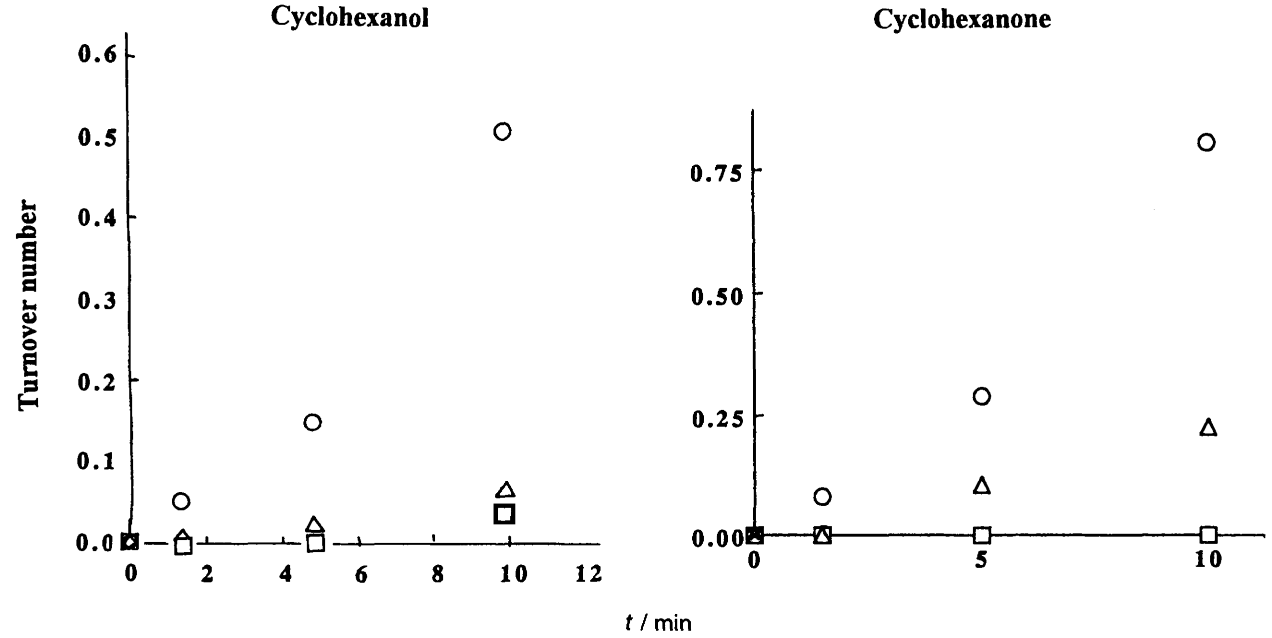


Fig. 3 Time courses of the turnover of the oxygenated products catalysed by iron(III) complexes at 0 °C: ○, L^4; △, L^3; □, L^1

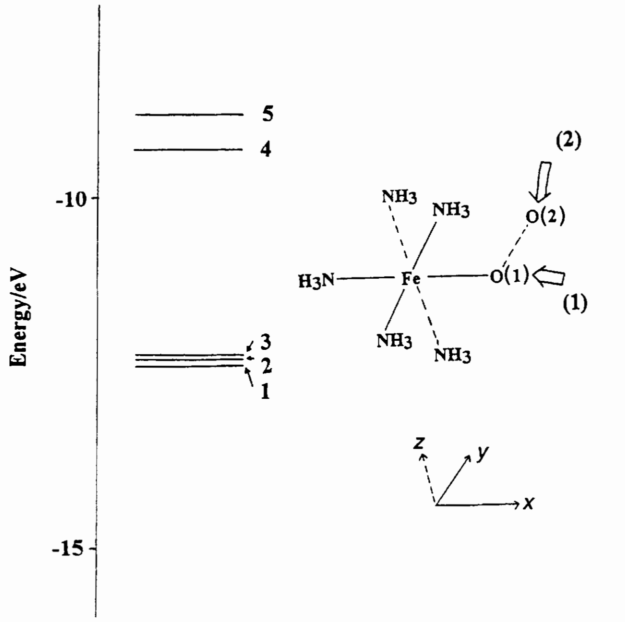


Fig. 5 Molecular orbital scheme for $[Fe(NH_3)_5(O_2)]^+$: Fe–N (NH_3), 2.00, Fe–O (peroxide) 2.00 and O–O (peroxide) 1.456 Å. Orbitals: 1–5, d orbitals; 1–3 are d_{xz}, d_{yz}, and d_{xy}. Approximate expression for orbital 5: 0.751 $d_{x^2-y^2}$ + 0.372 p_x[O(1)] + 0.226 p_z[O(1)] +0.185 p_z[O(2)] + 0.021p_x[O(2)]

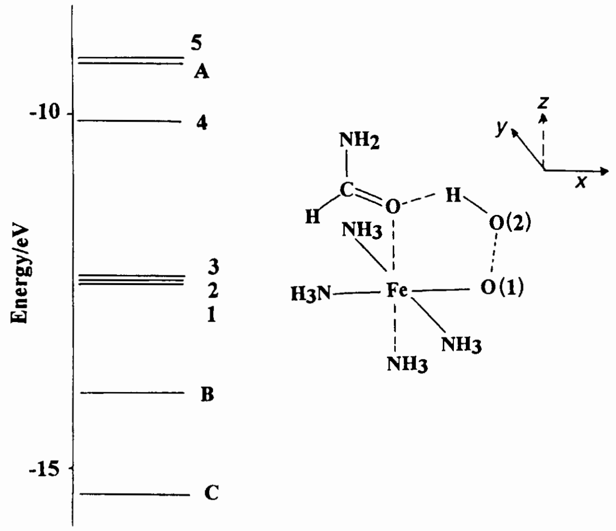
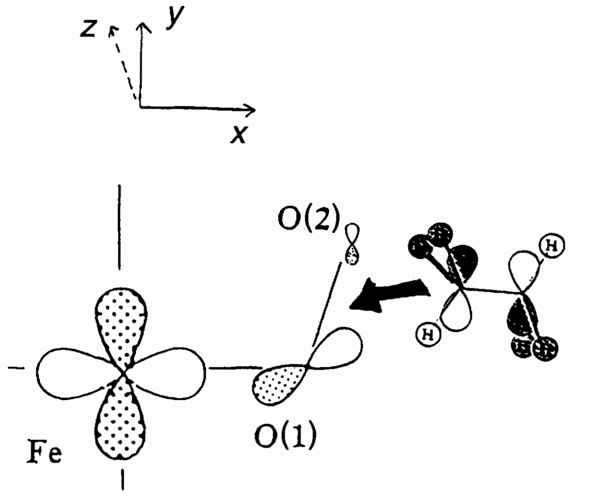


Fig. 6 Molecular orbital scheme for $[Fe(NH_3)_4(HCONH_2)(HO_2)]^{2+}$: Fe–N ($NH_3$) 2.00; Fe–O (amide) 2.165; Fe–O (peroxide) 2.00; O–O (peroxide ion) 1.422 and O (amide)-H (hydroperoxide) 1.338 Å. Orbitals: 1–5, d orbitals; 1–3 are d_{xz}, d_{yz} and d_{xy}. Expressions for orbitals: 5, 0.854 $d_{x^2-y^2}$ + 0.275 p_x[O(1)] + 0.173 p_z[O(1)] + 0.152 p_z[O(2)]; A, 0.508 p_y(amide oxygen) − 0.968 p_y(carbon atom)(π* of C=O); B, −0.437 p_x(amide oxygen) − 0.501 p_z(amide oxygen) + 0.335 p_x[O(1)] − 0.380 p_x[O(2)]; C, 0.440 p_x(amide oxygen) − 0.159 p_z(amide oxygen) + 0.541 p_x[O(1)] + 0.190 p_x[O(2)] − 0.125 $d_{x^2-y^2}$ + 0.218 d_{z^2}

hydroperoxide adduct in addition to the electrostatic interaction due to hydrogen bonding, and also activation of the peroxide ion. This indicates that adduct **I** may exhibit higher affinity for the bonding orbitals of the organic substrate, than that in the $[Fe(NH_3)_5(O_2)]^+$ complex. Such an interaction between a peroxide ion and a pyridine (py) ring was not indicated by EHMO calculations for $[Fe(NH_3)_4(py)(HO_2)]^{2+}$. Thus, it seems quite likely that in the cases of the L^1 and L^3 complexes the formation of a peroxide adduct having η^1 co-ordination mode may be less favourable due to steric repulsions (presence of CH of the pyridine ring) and the absence of electronic interaction between the peroxide ion and pyridine or morpholine ring, and thus may lead only to



Scheme 2

a (μ-η^1:η^1-peroxo)diiron(III) species, which is consistent with the negligible activities observed for these complexes in the oxygenation of cyclohexane.

Based on these facts, we would like to propose that the oxygenation reaction of cyclohexane catalysed by adduct **I** may proceed as follows. Adduct **I** exhibits an 'oxo-like reactivity', *i.e.* it acts as an electrophile (because orbital 5 in Fig. 6 is not doubly occupied), and interacts with the electrons of bonding orbitals of a substrate to give an oxygenated product with concomitant cleavage of the O–O bond in a concerted manner:[22] Fe^{III}–OOH + $C_6H_{12} \longrightarrow Fe^{III}$–OH + $C_6H_{11}OH$ (see Scheme 2; where the approach of highest occupied molecular orbital of the ethane molecule[23] to the O(1) region is depicted; the signs of the orbitals of the two compounds are the same).

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