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A discrete $\{Co_4(\mu_3\text{-}OH)_4\}^{4+}$ cluster with an oxygen-rich coordination environment as a catalyst for the epoxidation of various olefins†

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Using the sterically hindered terphenyl-based carboxylate, the tetrameric Co(II) complex $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]$ (**1**) with an asymmetric cubane-type core has been synthesized and fully characterized by X-ray diffraction, UV-vis spectroscopy, and electron paramagnetic resonance spectroscopy. Interestingly, the cubane-type cobalt cluster **1** with 3-chloroperoxybenzoic acid as the oxidant was found to be very effective in the epoxidation of a variety of olefins, including terminal olefins which are more challenging targeting substrates. Moreover, this catalytic system showed a fast reaction rate and high epoxide yields under mild conditions. Based on product analysis and Hammett studies, the use of peroxyphenylacetic acid as a mechanistic probe, $H_2{}^{18}O$-exchange experiments, and EPR studies, it has been proposed that multiple reactive cobalt-oxo species $Co^{V}{=}O$ and $Co^{IV}{=}O$ were involved in the olefin epoxidation.

1. Introduction

Metalloenzymes are well known to catalyze biologically important oxygenation reactions efficiently under mild conditions. To mimic such enzymatic actions, several transition metal-based catalysts have been recently synthesized and used to achieve O–O bond activation and subsequent oxygenations.[1] In this regard, iron and manganese porphyrins have been considered as the most successful catalysts for the oxidation reactions of various organic substrates.[1,2] On the other hand, the oxidation reaction studies of hydrocarbons by using cobalt complexes have been relatively less explored.[3] In these studies, cobalt(IV)-oxo[3] and a few cobalt(V)-oxo species[4] have been suggested to participate actively in the transfer of oxygen atoms with an oxidant, such as 3-chloroperoxybenzoic acid (MCPBA) and iodosylbenzene (PhIO).

Furthermore, oxo-bridged transition metal complexes with ancillary N- and O-donor ligands are of considerable interest to synthetic inorganic chemists because of their interesting structures as well as their magnetic, optical, and catalytic properties.[5–7] A few cubane-like cobalt(III) complexes have been known to catalyze the oxidation of some commercially important organic substrates. For example, the cobalt(III)-oxo cubane clusters, $Co_4O_4(O_2CMe)_4(py)_4$, have shown efficient catalytic activities for the aerobic oxidation of ethylbenzene and *p*-xylene.[5a] Also, the tetrameric cubane-like complex $[Co_4O_4(O_2CC_6H_4\text{-}X)_4(py)_4]$ was examined as a catalyst for the homogeneous *t*-BuOOH oxidation of benzyl alcohols under mild conditions.[6] Chakrabarty *et al.* demonstrated the effectiveness of a cobalt(III) complex, $Co_4^{III}(\mu_3\text{-}O)_4(\mu\text{-}O_2CCH_3)_4$(4-CNpy)$_4$, for the catalytic oxidation of α-pinene by dioxygen in aqueous media.[7] They proposed an oxidation mechanism where both cobalt(III) and cobalt(IV) could be involved in the catalytic cycle. Although a few cubane-like cobalt(III) complexes have been reported to catalyze the oxidation of some organic substrates, they have only shown reactivity for easy-to-oxidize substrates such as benzyl alcohols, styrene, ethylbenzene and α-pinene.[3–7] In order to further develop a new cubane-type tetracobalt cluster capable of being applied to the catalytic hydrocarbon oxidation of a wide range of substrates such as terminal and internal olefins, we synthesized the title complex and examined the catalytic epoxidation of various olefins under mild conditions.

Herein, we report the synthesis and full characterization of a tetranuclear Co(II) complex with the general formula $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CR)_2(\mu\text{-}OTf)_2(Py)_4]$ (**1**), which comprises an asymmetric cubane-type core housed within two sterically bulky carboxylate ligands. In addition, **1** was found to be robust, readily available and active in epoxidation reactions of

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various olefins. Moreover, **1** is the first cubane-type cobalt catalyst to afford high conversions and epoxide yields in the epoxidation of terminal olefins. Based on product analysis, $H_2{}^{18}O$ experiments, Hammett studies, and the use of peroxyphenylacetic acid (PPAA) as a mechanistic probe, $Co^{V}{=}O$ and $Co^{IV}{=}O$ species were proposed to be possible reactive intermediates responsible for the olefin epoxidation.

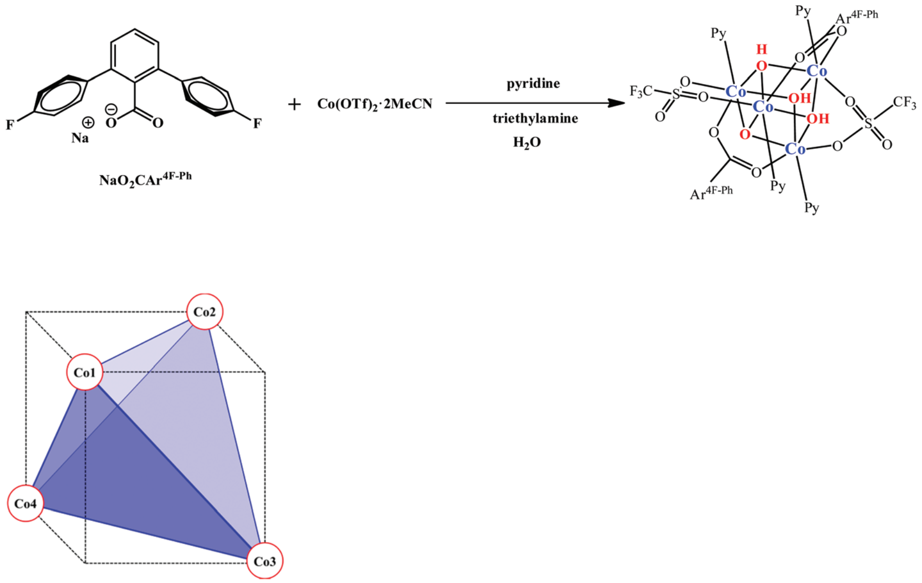
2. Results and discussion

Synthesis

An intriguing report by Lee *et al.* described the successful preparation of hydroxo-bridged tetranuclear iron complexes with combined ligand sets consisting of pyridine derivatives and bulky carboxylates, which led us to prepare the hydroxo-bridged cobalt cubane-type clusters *via* a similar synthetic route.[8] To prepare Co(II) analogues of the reported tetranuclear iron complexes, the reaction was examined using stoichiometric reagents (Scheme 1). The reaction between $NaO_2CAr^{4F\text{-}Ph}$, $Co(OTf)_2{\cdot}2CH_3CN$, pyridine, triethylamine and H_2O in THF under argon afforded red block crystals of the neutral $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]$ complex (**1**) in moderate yield (60%) (Scheme 1).

Characterization

The structure of complex **1** was determined by X-ray crystallography (Fig. 1), and the crystallographic data and the selected bond lengths and angles have been listed in Tables 1–3, respectively. The compound had a slightly distorted cubic-type $\{Co_4(\mu_3\text{-}OH)_4\}$ unit with interpenetrating Co_4 and $(OH)_4$ disphenoids. The Co–N distances from each Co atom ranged from 2.112(3) Å to 2.127(3) Å, as summarized in Table 3. Hormillosa *et al.* reported so-called Bond Valence Sum (BVS), in which the average distance between metal cations and ligands can be used to estimate the oxidation state of the metal cation.[9] The calculated BVS values in the present case were distributed between 2.035 and 2.065, indicating that the oxidation states of Co cations in the cubane were all 2+ (Table 3). All of the Co(II) sites had slightly distorted octahedral geometries with a NO5 donor atom set, composed of pyridine, triflate, and carboxylate, as well as three hydroxo ligands, each bridging three Co atoms. The assignment of hydroxide to oxo was confirmed by the observed Co–O distances, ranging from 2.050(2) to 2.265(3) Å, and also by the refinement of the associated hydrogen atoms from the difference electron density maps. Comparable $Co\text{–}O_{hydroxo}$ distances occur in other high-spin cobalt(II) complexes.[10] Organized variations in the Co⋯Co distances were observed, depending on the nature of the bridging ligands. There were three different types of $\{Co_2(\mu\text{-}OH)_2\}$ units in the cubane: triply bridged $\{Co_2(\mu\text{-}OH)_2(\mu\text{-}O_2CAr^{4F\text{-}Ph})\}$, triply bridged $\{Co_2(\mu\text{-}OH)_2(\mu\text{-}OTf)\}$ and doubly bridged $\{Co_2(\mu\text{-}OH)_2(Py)\}$, thus the six Co⋯Co separations can be grouped into three different lengths – distributed around 3.0 Å, 3.1 Å and 3.2 Å – resulting in a distorted cubic core composed of $\{Co_4(\mu_3\text{-}OH)_4\}$. Intermetallic Co⋯Co distances decreased with increasing numbers of bridging ligands; the intermetallic distances in the $\{Co_2(\mu\text{-}OH)_2(\mu\text{-}O_2CAr^{4F\text{-}Ph})\}$ units were 0.1 Å shorter than the $\{Co_2(\mu\text{-}OH)_2(\mu\text{-}OTf)\}$ units and 0.2 Å shorter than doubly bridged $\{Co_2(\mu\text{-}OH)_2(Py)\}$ units. The Co–O–Co angles were closely distributed, ranging between 77.79(9)° and 85.58 (8)° (Table S1†). As a trend, a decrease in the Co⋯Co distances was accompanied by a decrease in the Co–O–Co bond angles in the $\{Co_2(\mu\text{-}OH)_2\}$ motifs. The elec-



Scheme 1 Synthesis of $\{Co_4(\mu_3\text{-}OH)_4\}^{4+}$ cluster **1**.

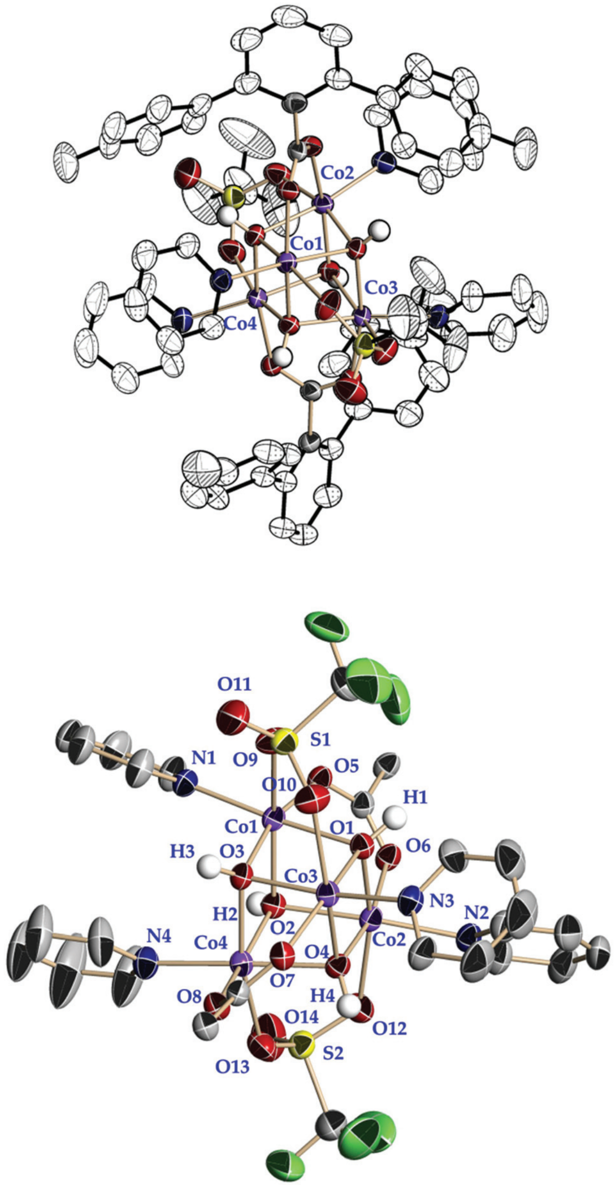


Fig. 1 (top) ORTEP drawings of the $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]$ cluster, showing 50% probability thermal ellipsoids. (top) The non-hydroxo hydrogen atoms are omitted for clarity. (bottom) The aromatic rings of the $Ar^{4F\text{-}Ph}CO_2^-$ ligands and the non-hydroxo hydrogen atoms are omitted for clarity.

tronic spectrum of the cobalt complex recorded in CH_2Cl_2 solution is shown in Fig. S1.† The central peak at 531 nm (ε = 150 M^{-1} cm^{-1}) is a characteristic feature of high-spin Co(II) ions. To understand the magnetic properties of the distorted cube (**1**) with 4 octahedral d^7 ions located within the steric bulk of the terphenyl-based ligands, magnetic susceptibility by the Evans method was determined at 297 K (see the ESI†), resulting in 4.61 (B.M. per Co atom). It reiterates that Co(II) ions are high-spin d^7, considering that experimental magnetic moments for octahedral Co(II) high-spin complexes are distributed over 4.3–5.2 B.M.[11]

Table 1 X-ray crystallographic data for the $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]\cdot 0.5(CH_3CH_2)_2O\cdot 0.5CH_2Cl_2$ complex

Formula	$C_{62.5}H_{52}ClCo_4F_{10}N_4O_{14.5}S_2$
Formula weight, g mol^{-1}	1616.37
T, K	293(2)
Radiation, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	12.8536(6)
b, Å.	14.3535(8)
c, Å	20.0526(11)
α, °	95.450(2)
β, °	105.838(2)
γ, °	93.734(2)
V, $Å^3$	3527.0(3)
Z	2
ρ_{calc}, g cm^{-3}	1.522
μ, mm^{-1}	1.111
$R_1{}^a$	0.0519
$wR_2{}^b$	0.1607
Goodness-of-fit on F^2	1.063
Reflections collected	17 602

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

Table 2 Selected interatomic distances (Å) and angles (°) for the $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]\cdot 0.25CH_2Cl_2$ complex

Co(1)–O(1)	2.117(2)	Co(3)–O(1)	2.069(2)
Co(1)–O(2)	2.076(2)	Co(3)–O(3)	2.084(2)
Co(1)–O(3)	2.062(2)	Co(3)–O(4)	2.075(2)
Co(1)–O(5)	2.063(2)	Co(3)–O(7)	2.087(2)
Co(1)–O(9)	2.209(3)	Co(3)–O(1)	2.265(3)
Co(1)–N(1)	2.118(3)	Co(3)–N(3)	2.115(3)
Co(2)–O(1)	2.092(2)	Co(4)–O(2)	2.050(2)
Co(2)–O(2)	2.107(2)	Co(4)–O(3)	2.083(2)
Co(2)–O(4)	2.056(2)	Co(4)–O(4)	2.103(2)
Co(2)–O(6)	2.052(2)	Co(4)–O(8)	2.058(2)
Co(2)–O(12)	2.246(3)	Co(4)–O(13)	2.216(3)
Co(2)–N(2)	2.112(3)	Co(4)–N(4)	2.127(3)
Co(1)···Co(2)	3.0283(6)	O(1)–Co(1)–O(2)	85.55(8)
		O(1)–Co(1)–O(3)	81.62(8)
Co(1)···Co(3)	3.1348(6)	O(2)–Co(1)–O(3)	78.77(9)
		O(1)–Co(2)–O(2)	85.41(8)
Co(1)···Co(4)	3.1946(6)	O(4)–Co(2)–O(1)	77.79(9)
		O(4)–Co(2)–O(2)	82.09(8)
Co(2)···Co(3)	3.2253(6)	O(1)–Co(3)–O(3)	82.25(8)
		O(1)–Co(3)–O(4)	77.88(9)
Co(2)···Co(4)	3.1199(6)	O(3)–Co(3)–O(4)	85.58(8)
		O(2)–Co(4)–O(3)	78.90(9)
Co(3)···Co(4)	3.0164(6)	O(2)–Co(4)–O(4)	82.33(8)
		O(3)–Co(4)–O(4)	84.90(8)

Table 3 Average distances of Co–O bonds and Co–N bonds of each metal site and calculated BVS values

	Average value of Co–**O** bond distances	Co–**N** bond distance	BVS calc. values
Co(1)	2.105	2.118	2.065
Co(2)	2.111	2.112	2.059
Co(3)	2.116	2.115	2.035
Co(4)	2.084	2.216	2.054

Table 4 Olefin epoxidations by MCPBA with the cubane-type cobalt cluster **1** in CH_2Cl_2/CH_3CN (1 : 1) at room temperature[a]

Entry	Substrate	Product	Conversion[b] (%)	Yield[b] (%)
1	Cyclopentene	Epoxide	82.0 ± 1.4	74.5 ± 3.1
2	Cycloheptene	Epoxide	98.5 ± 1.3	97.9 ± 2.2
3	Cyclooctene	Epoxide	99.2 ± 0.5	92.0 ± 2.1
4	Cyclohexene	Epoxide	88.2 ± 0.6	61.5 ± 2.4
		2-Cyclohexene-1-one		4.1 ± 0.1
		2-Cyclohexene-1-ol		1.5 ± 0.1
5	1-Hexene	Epoxide	72.6 ± 5.1	67.8 ± 0.6
6	1-Octene	Epoxide	59.7 ± 7.4	50.7 ± 4.0
7	*cis*-2-Hexene	*cis*-Oxide	79.5 ± 2.8	62.4 ± 0.5
		trans-Oxide		17.1 ± 1.0
8	*trans*-2-Hexene	*trans*-Oxide	78.1 ± 0.4	73.7 ± 4.2
9	*cis*-2-Octene	*cis*-Oxide	86.6 ± 1.5	63.6 ± 1.5
		trans-Oxide		16.1 ± 0.1
10	*trans*-2-Octene	*trans*-Oxide	79.3 ± 0.7	64.0 ± 0.7
11	Styrene	Epoxide	82.0 ± 1.6	42.8 ± 1.4
		Benzaldehyde		5.5 ± 0.1
		Phenylacetaldehyde		—
12	*cis*-Stilbene	*cis*-Stilbene oxide	93.2 ± 1.1	10.3 ± 0.4
		trans-Stilbene oxide		33.5 ± 1.6
		Benzaldehyde		15.9 ± 0.1
		2-Phenylacetophenone		8.7 ± 0.5
13	*trans*-Stilbene	*trans*-Stilbene oxide	93.4 ± 0.1	40.6 ± 4.1
		Benzaldehyde		20.6 ± 1.4
		2-Phenylacetophenone		6.3 ± 0.4

[a] Reaction conditions: olefin (0.035 mmol), catalyst (0.001 mmol), MCPBA (0.10 mmol), and solvent (1 mL, CH_2Cl_2/CH_3CN = 1 : 1). [b] Based on the substrate.

Olefin epoxidation reaction catalyzed by 1

We conducted the catalytic epoxidation of various olefins with MCPBA in the presence of the cubane-type cobalt cluster **1** under mild conditions. MCPBA (0.1 mmol) was added to a mixture of substrate (0.035 mmol), catalyst **1** (0.001 mmol), and solvent (CH_3CN/CH_2Cl_2, 1 : 1 v/v; 1 mL). The mixture was stirred for 10 min at room temperature. Control experiments suggested that direct oxidation of the substrate by MCPBA was negligible and that **1** was stable enough during the catalytic reactions according to the UV-vis spectroscopic study. The results of the epoxidation reaction are summarized in Table 4. Cyclic olefins such as cyclopentene, cycloheptene, and cyclooctene were oxidized to the corresponding epoxides in good yields (74.5–97.9%, entries 1–3), with conversions ranging from 82.0 to 99.2%. Meanwhile, cyclohexene (entry 4) afforded cyclohexene oxide (61.5%) as a major product and small amounts of 2-cyclohexen-1-one (4.1%) and 1-cyclohexen-1-ol (1.5%).[12] Although terminal olefins such as 1-hexene and 1-octene (entries 5 and 6) are well known as difficult-to-oxidize substrates,[13,14] their corresponding epoxides were obtained in good yields (67.8% and 50.7%, respectively). *cis*-2-Hexene and *cis*-2-octene were used to probe the epoxidation stereochemistry, which were oxidized mainly to *cis*-2-hexene oxide and *cis*-2-octene oxide (62.4% and 63.6%; entries 7 and 9) in addition to some amounts of *trans*-2-hexene oxide (17.1%) and *trans*-2-octene oxide (16.1%), respectively. These results demonstrated that a stereochemical retention of 57.0% for *cis*-2-hexene and 60.0% for *cis*-2-octene was retained in this epoxidation reaction. Styrene was oxidized to styrene epoxide (42.8%; entry 11) with a small amount of benzaldehyde (5.5%). While *cis*-stilbene was oxidized to *cis*-stilbene oxide (10.3%; entry 12) and *trans*-stilbene oxide (33.5%) along with some benzaldehyde (15.9%) and 2-phenylacetophenone (8.7%), *trans*-stilbene was converted to *trans*-stilbene oxide (40.6%; entry 13) as a major product with minor amounts of benzaldehyde (20.6%) and 2-phenylacetophenone (6.3%). In the case of olefins having aromatic rings, the substrates gave by-products of aldehyde and ketone in moderate yields and showed very low stereochemical retention. These results demonstrated that either the peroxyl radical or oxocobalt(IV) as the epoxidizing agent might be partially involved in this catalytic reaction. These species were expected to generate non-stereospecific or radical-induced rearranged products from the epoxidation reaction of aromatic olefins, based on previous reports.[12b,15–17] Another possibility is that the $\mathrm{Co(IV)\text{-}OCR_2CR_2^{\bullet}}$ intermediate with a long lifetime generated from the reaction of *cis*-olefin with $\mathrm{Co^{V}{=}O}$ species may rotate to produce *trans*-epoxide. Therefore, all the combined results suggested that two different oxidants, *viz.* $\mathrm{Co^{V}{=}O}$ and $\mathrm{Co^{IV}{=}O}$, might be generated in these catalytic reactions and the $\mathrm{Co^{IV}{=}O}$ complex would be responsible for the non-stereoretentive portion of the epoxidation reaction.

Terminal olefins have been considered as difficult-to-oxidize olefins because of their electron-deficient nature,[13,14] while their corresponding products 1,2-epoxides are known as versatile starting materials for the synthesis of more complicated compounds. Therefore, we investigated the terminal olefin epoxidation by using **1**, because 1-hexene and 1-octene were reasonably oxidized to their corresponding epoxides. The

Table 5 Terminal olefin epoxidation by MCPBA with the cubane-type cobalt cluster **1** in CH_2Cl_2/CH_3CN (1 : 1) at room temperature[a]

Entry	Substrate	Product	Conversion[b] (%)	Yield[b] (%)
1	1-Hexene	1,2-Epoxyhexane	72.6 ± 5.1	67.8 ± 0.6
2	1-Octene	1,2-Epoxyoctane	59.7 ± 7.4	50.7 ± 4.0
3	1-Nonene	1,2-Epoxynonane	52.2 ± 4.4	37.3 ± 0.8
4	1-Decene	1,2-Epoxydecane	52.4 ± 0.9	35.9 ± 1.2
5	1-Undecene	1,2-Epoxyundecane	77.0 ± 2.0	45.4 ± 1.2
6	1-Dodecene	1,2-Epoxydodecane	77.6 ± 0.1	50.3 ± 0.8
7	1-Tridecene	1,2-Epoxytridecane	75.6 ± 0.1	59.5 ± 0.3
8	1-Tetradecene	1,2-Epoxytetradecane	76.4 ± 0.2	41.6 ± 0.6
9	1-Pentadecene	1,2-Epoxypentadecane	79.1 ± 0.4	51.5 ± 1.7
10	1-Hexadecene	1,2-Epoxypentadecane	48.4 ± 0.5	43.0 ± 8.9
11	1-Octadecene	1,2-Epoxypentadecane	46.5 ± 2.7	40.8 ± 3.6
12	Vinylcyclohexane	2-Cyclohexyloxirane	57.1 ± 1.0	31.5 ± 0.5

[a] Reaction conditions: olefin (0.035 mmol), catalyst (0.001 mmol), MCPBA (0.10 mmol), and solvent (1 mL, $CH_2Cl_2/CH_3CN = 1:1$). [b] Based on the substrate.

results are summarized in Table 5. All of the terminal olefins were oxidized to the corresponding epoxides in moderate yields (31.5–67.8%), with conversions in the range of 46.5–79.1%, indicating that our catalytic system could be useful for the epoxidation reaction of a variety of terminal olefins. To the best of our knowledge, **1** is the first cubane-type cobalt catalyst to afford high conversions and epoxide yields in the epoxidation of terminal olefins by MCPBA.[5–7]

Competition experiments of styrene and *para*-substituted styrenes for the Hammett plot

In order to examine the nature of the reactive species responsible for the epoxidation reaction, we studied the influence of substituent electronic effects on the reaction rate using styrene and four *para*-substituted styrenes. The analysis of a Hammett plot showed a ρ value of −0.49, indicating that the active oxidant was electrophilic (Fig. 2). This value is comparable to those reported for Mn(salen) ($\rho = -0.3$),[17c] Mn^{III} tetraphenylporphyrin ($\rho = -0.3$),[18] and $Mn(^{M,Me}PyTACN)(CF_3SO_3)_2$ ($\rho = -0.37$).[19]

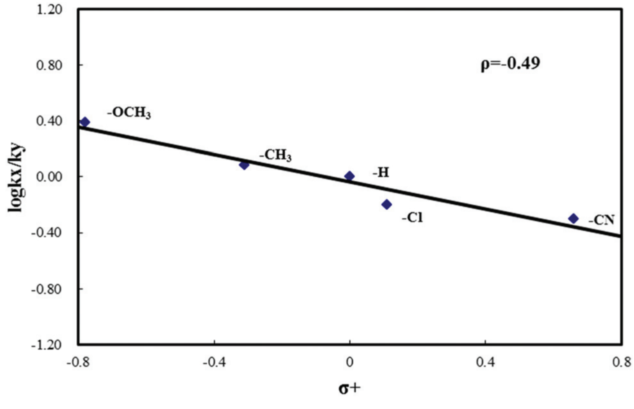


Fig. 2 Hammett plot for selective reactivities of styrene to *para*-substituted styrenes by the cubane-type cobalt cluster **1** with MCPBA.

$H_2{}^{18}O$ experiments

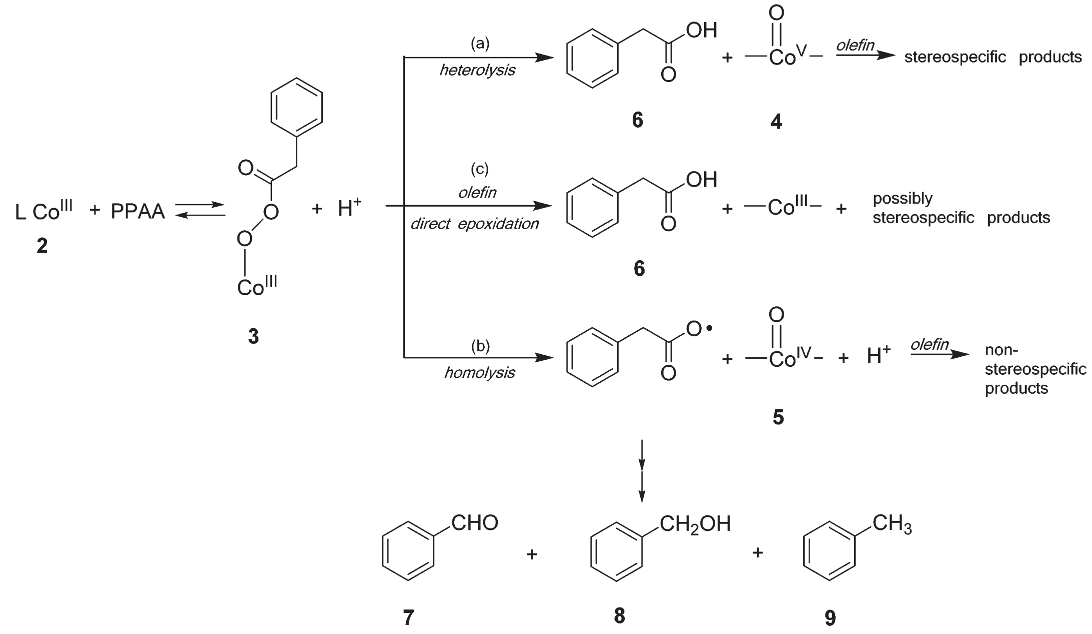
To further investigate the mechanism of olefin epoxidation, we carried out isotope labeling experiments using $H_2{}^{18}O$, because ^{18}O-labeling experiments are commonly used in the studies of reaction mechanisms to test the involvement of a high-valent metal-oxo intermediate in metal-mediated oxygen atom transfer reactions.[20–22] Epoxidation of cyclohexene by **1** and MCPBA was conducted in the presence of a large excess (100–400 equiv.) of $H_2{}^{18}O$ to the substrate in a mixture of CH_3CN and CH_2Cl_2 (v/v, 1 : 1). GC-MS analysis of the products showed no ^{18}O-incorporation into cyclohexene oxide from $H_2{}^{18}O$. This result suggested two possibilities: one is that the rate of oxygen atom transfer from Co-oxo species to olefin might be faster than the oxygen exchange rate between Co-oxo species and $H_2{}^{18}O$, and the other is that the direct olefin epoxidation by Co^{III}-OOC(O)R species may occur before its O–O bond cleavage.

EPR studies

In order to figure out the oxidation state of cobalt ions after the epoxidation reaction, we carried out the electron paramagnetic resonance (EPR) study. The EPR spectrum of the starting complex was silent (Fig. S2†), indicating that there is a magnetic exchange between the four Co(II) ions. Moreover, complex **1** obtained 5 s after the catalytic epoxidation reaction also showed a silent EPR spectrum. This result assumed that the Co^{II} complex might be first oxidized to a Co^{III} complex by MCPBA, and then the Co^{III} complex acted as a catalyst. Furthermore, we carried out EPR studies at low temperature in order to trap any possible intermediates, such as $Co^{IV}{=}O$ species. An intermediate state frozen 5 seconds after complex **1** was mixed with MCPBA at −40 °C in a mixture of CH_3CN and CH_2Cl_2 (v/v, 1 : 1) showed silent EPR signals, which indicated that it was considerably difficult to capture the possible reactive species with the EPR spectroscopy method.

Product distribution of the O–O bond cleavage of PPAA with catalyst 1

PPAA has often been used as a mechanistic probe to identify the cleavage mode of the peracid O–O bond through quantitative determination of the degradation products derived from the reaction of the catalyst and PPAA.[15,16,21,22] While heterolytic cleavage of the O–O bond of the Co-acylperoxo species **3** generated phenylacetic acid (PAA, **6**; pathway (a) of Scheme 2), the O–O bond is cleaved homolytically to form an acyloxyl radical, which afforded benzaldehyde (**7**), benzyl alcohol (**8**), and toluene (**9**) *via* a rapid β-scission of the acyloxyl radical (pathway (b) of Scheme 2).[16] The direct oxidation of the substrate by the Co-acylperoxo intermediate **3** gave PAA (**6**; pathway (c) of Scheme 2). For a control test, the reaction of catalyst **1** with PPAA was carried out in the absence of a substrate (entry 1, Table 6). The results showed that the heterolytic cleavage product, phenylacetic acid (73.3% based on PPAA), and the homolytic cleavage products, benzaldehyde (17.0%) and benzyl alcohol (1.2%), were formed. This result demonstrated that the intermediate Co^{III}-OOC(O)R species underwent the partition of the heterolysis (80.1%) and the homolysis (19.9%) to give high-valent $Co^{V}{=}O$ (**4**) and $Co^{IV}{=}O$ (**5**) species. Next, in order to investigate the concentration effects of an easy-to-oxidize substrate, cyclohexene, we carried out the epoxidation reaction of it by **1** with PPAA.[12a,15,16] When the concentration of cyclohexene increased gradually from 0 to 160 mM, heterolysis increased slightly from 80 to 87 (entries 1–5). This result implied that the Co^{III}-OOC(O)R species **3** might be a little involved in the olefin epoxidation reaction



Scheme 2 Possible degradation pathway of PPAA by the Co(III) complex.

Table 6 Yield of products derived from PPAA mediated by the cubane-type cobalt cluster **1** in the absence and presence of cyclohexene in a mixture of CH_3CN/CH_2Cl_2 (1 : 1) at room temperature[a]

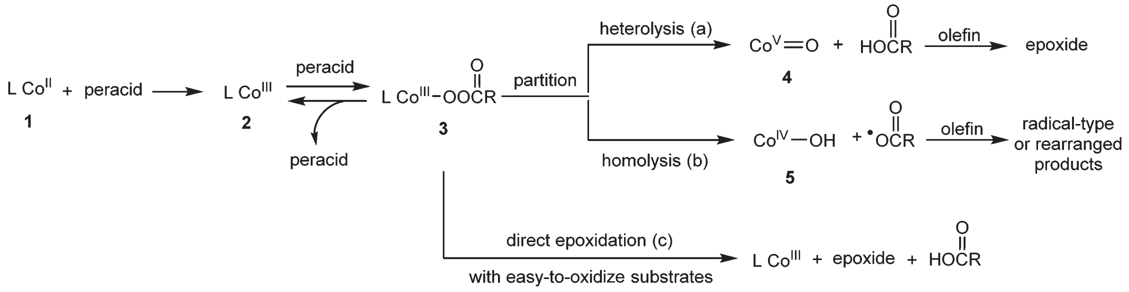
Entry	Cyclohexene [mM]	Heterolysis[b] **6**	Homolysis[b] **7**	**8**	**9**	Hetero/Homo [**6**/(**7** + **8** + **9**)][c]	Oxidation products[d] Oxide	Ol	One
1	0	73.3 ± 0.4	17.0 ± 0.4	1.2 ± 0.4	—	4.02 (80.1/19.9)	—	—	—
2	20	76.2 ± 0.7	14.1 ± 0.1	1.3 ± 0.0	—	4.95 (83.2/16.8)	28.4 ± 0.7[e]	6.8 ± 0.2[e]	3.4 ± 0.0[e]
3	40	81.5 ± 0.3	13.8 ± 0.0	1.4 ± 0.1	—	5.36 (84.3/15.7)	20.2 ± 0.6[e]	5.0 ± 0.0[e]	2.7 ± 0.1[e]
4	80	80.3 ± 1.1	11.4 ± 0.1	1.4 ± 0.2	—	6.27 (86.2/13.8)	23.4 ± 0.4[b]	7.2 ± 0.1[b]	4.0 ± 0.1[b]
5	160	86.7 ± 2.3	10.8 ± 0.1	2.4 ± 1.1	—	6.57 (86.8/13.2)	36.2 ± 3.0[b]	11.8 ± 0.1[b]	7.5 ± 0.6[b]

[a] Reaction conditions: substrate (0–0.16 mmol), catalyst (0.001 mmol), PPAA (0.04 mmol), and solvent (1 mL, CH_3CN/CH_2Cl_2 = 1 : 1). [b] Based on PPAA. [c] **6–9** indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [d] Ol, one, and oxide indicate 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and cyclohexene oxide, respectively. [e] Based on cyclohexene.

Table 7 Yield of products derived from PPAA mediated by the cubane-type cobalt cluster **1** in the absence and presence of 1-octene in a mixture of CH_3CN/CH_2Cl_2 (1 : 1) at room temperature[a]

			Homolysis[b]				
Entry	1-Octene [mM]	Heterolysis[b] **6**	**7**	**8**	**9**	Hetero/Homo [**6**/(**7** + **8** + **9**)][c]	Oxidation products[d] 1-Octene oxide
1	0	73.3 ± 0.4	17.0 ± 0.4	1.2 ± 0.4	—	4.02 (80.1/19.9)	—
2	20	80.3 ± 5.0	20.3 ± 0.9	1.4 ± 0.2	—	3.70 (78.7/21.3)	7.1 ± 0.3
3	40	78.9 ± 0.5	19.9 ± 0.3	1.2 ± 0.1	—	3.74 (78.9/21.1)	4.8 ± 0.2
4	80	77.0 ± 0.4	19.1 ± 0.6	1.3 ± 0.3	—	3.77 (79.0/21.0)	6.1 ± 0.2
5	160	86.0 ± 1.3	19.3 ± 0.7	3.3 ± 2.1	—	3.80 (79.2/20.8)	10.1 ± 1.4

[a] Reaction conditions: substrate (0–0.16 mmol), catalyst (0.001 mmol), PPAA (0.04 mmol), and solvent (1 mL, CH_3CN/CH_2Cl_2 = 1 : 1). [b] Based on PPAA. [c] **6–9** indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [d] Based on 1-octene.



Scheme 3 Plausible mechanism for the olefin epoxidation reaction by **1** with peracids.

when the concentration of cyclohexene was very high. We changed the substrate from cyclohexene to a difficult-to-oxidize olefin, 1-octene, to examine the cleavage mode of PPAA on the type of substrate.[22] The ratio (80 : 20) of the heterolysis and the homolysis was fairly constant, depending on the change of the 1-octene concentration (entries 1–5, Table 7). These results suggested that the Co^{III}-OOC(O)R species would not be involved in the epoxidation of 1-octene, even at its high concentration.

It can also be mentioned that we have observed similar reactivity patterns between this cubane-type cobalt-cluster system and a mononuclear nonheme cobalt(III) complex previously reported.[15a] The similar reactivity patterns suggest that the simultaneous operation of the two active oxidants, Co^{V}=O or Co^{IV}=O species, might prevail in all cobalt-catalyzed olefin epoxidations.

Mechanistic comments

Based on our mechanistic studies, the most plausible mechanism for the formation of the reactive species responsible for olefin epoxidation could be sketched as shown in Scheme 3. First, the cobalt(II) cluster **1** was oxidized to a cobalt(III) cluster by a peracid molecule, which further reacted with another peracid molecule to form an initial cobalt-acylperoxo intermediate (Co^{III}-OOC(O)R, **3**). Then, **3** underwent either a heterolysis or a homolysis to afford Co^{V}=O or Co^{IV}=O species, respectively. The resulting Co^{V}=O intermediate formed from heterolysis might be responsible for the olefin epoxidation that showed a high yield of epoxide and a high stereochemical retention, whereas a Co^{IV}=O complex generated *via* homolysis was ascribed to a radical-type oxidation that showed the formation of allylic oxidation products and a loss of stereospecificity. The direct epoxidation of olefin by Co-OOR species occurred to a lesser extent with only an easy-to-oxidize substrate, such as cyclohexene. Therefore, the oxidants Co^{V}=O and Co^{IV}=O might act simultaneously as key active intermediates in the olefin epoxidation reaction catalyzed by the cubane-type cobalt cluster **1**.

3. Conclusions

We have synthesized a tetranuclear Co(II) complex **1** with an asymmetric cubane-type core using the bulky carboxylate ligand, for the first time, and studied the oxidation of a wide range of olefins using the cluster **1**. In particular, the catalyst **1** was effective for the epoxidation of terminal olefins, the so-called difficult-to-oxidize substrate. Reactivity and Hammett studies, EPR, $H_2{}^{18}O$ exchange experiments, and the use of PPAA as a mechanistic probe suggested that Co(V)=O and Co(IV)=O operated simultaneously as active oxidant species in the epoxidation reactions. Under extreme conditions, in which the concentration of an active substrate was very high, the Co(III)-OOC(O)R species might also be a possible reactive species for epoxidation. Moreover, similar reactivity patterns between this cubane-type cobalt-cluster system and the previously reported mononuclear nonheme cobalt(III) complex suggested that $Co^{V}{=}O$ or $Co^{IV}{=}O$ species might operate simultaneously as key reactive oxidants in all the cobalt-catalyzed olefin epoxidations. Our future work will focus on observing spectroscopic evidence for the high-valent cobalt-oxo species (Co(V)=O and Co(IV)=O) described herein.

4. Experimental section

General

Olefins, epoxides, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, benzaldehyde, acetonitrile, dichloromethane, dodecane, MCPBA (65%), and $H_2{}^{18}O$ (97% ^{18}O enrichment) were purchased from Aldrich Chemical Co. and were used without further purification. PPAA was synthesized according to the literature methods.[12a] All manipulations for the synthesis of the cubane cluster **1** were performed under anaerobic conditions. All the solvents were distilled and dried prior to use: CH_2Cl_2 was distilled over CaH_2, and tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over a mixture of sodium and benzophenone under a nitrogen atmosphere. The *m*-terphenyl-based carboxylate ligand, 4,4″-fluoro-[1,1′:3′,1″-terphenyl]-2′-carboxylic acid ($HO_{2C}Ar^{4F\text{-}Ph}$), was prepared according to literature procedures.[23] The sodium salt ($NaO_2CAr^{4F\text{-}Ph}$) of this carboxylic acid was prepared by treating a MeOH solution of the free acid with 1 equiv. NaOH and removing the volatile fractions under reduced pressure.

Instrumentation

Product analysis for olefin epoxidation, PPAA experiments, and ^{18}O incorporation reactions of cyclohexene oxide were conducted by using a PerkinElmer gas chromatograph equipped with a FID detector and a 30 m capillary column (Hewlett-Packard, DB-5 or HP-FFAP). IR spectra were recorded on a Bio-Rad FTS 135 spectrometer as KBr pellets. UV-vis spectra were recorded with a PerkinElmer model Lambda 2S UV/Vis spectrometer. SW-EPR spectra were recorded at 5 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM).

Synthesis of $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CAr^{4F\text{-}Ph})_2(\mu\text{-}OTf)_2(Py)_4]$ (1)

To a rapidly stirred THF (5 mL) solution of $Co(OTf)_2{\cdot}2MeCN$ (271 mg, 0.617 mmol) was added $NaO_2CAr^{4F\text{-}Ph}$ (0.100 g, 0.308 mmol). After 1 h of stirring, pyridine (Py, 68.3 mg, 0.863 mmol) and triethylamine (62.4 mg, 0.617 mmol) were sequentially added. Argon-saturated H_2O (11.1 μL, 0.617 mmol) was added after 30 min. After 1 h of stirring, the volatile portion of the solution was removed under reduced pressure. The solid portion was dissolved in CH_2Cl_2 (3 mL), and the resulting inhomogeneous dispersion was filtered through Celite. Red color block crystals of **1** were isolated upon vapor diffusion of Et_2O into the filtrate after 4 days. FT-IR (KBr, cm^{-1}) 3651 (w), 3637 (w), 3446 (b), 3067 (w), 3001 (w), 2818 (w), 2741 (w), 1606 (m), 1579 (m), 1560 (m), 1519 (w), 1488 (w), 1447 (m), 1412 (w), 1378 (w), 1291 (s), 1244 (s), 1223 (s), 1163 (m), 1074 (w), 1032 (s), 1011 (m), 848 (w), 837 (w), 821 (w), 803 (m), 790 (w), 776 (w), 750 (w), 743 (w), 719 (w), 701 (m), 689 (m), 638 (s), 612 (m), 586 (w), 575 (w). Anal. Calcd for **1** or $Co_4C_{60}H_{46}F_{10}N_4O_{14}S_2$: C, 46.89; H, 3.02; N, 3.65. Found: C, 46.78; H, 3.10; N, 3.62.

X-Ray single crystal structural analysis

A single crystal was mounted at room temperature on the tips of quartz fibers, coated with Paratone-N oil, and cooled under a stream of cold nitrogen. Intensity data were collected on a Bruker CCDC area diffractometer running the SMART software package,[24] with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by using the SHELXTL software package.[25] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the bridged hydroxo O–H groups in the core were assigned from the electron density map; all other hydrogen atoms were assigned at idealized positions and given thermal parameters equivalent to 1.2 times the thermal parameter of the carbon atom to which they were attached. Data collection and experimental details of the complex are summarized in Table 1, and relevant interatomic distances and angles are listed in Tables 2 and 3. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference number for **1** is 1408240).

Catalytic olefin epoxidations by MCPBA in the presence of the cobalt cubane cluster 1

MCPBA (0.1 mmol) was added to a mixture of substrate (0.035 mmol), cubane-type cobalt cluster **1** (0.001 mmol), and solvent (CH_3CN/CH_2Cl_2, 1 : 1 v/v; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. Dodecane was used as an internal standard to quantify the yields of the products and conversions of the substrates. All reactions were run at least in triplicate, and the average conversions and product yields are presented. Conversions and product yields were calculated with respect to substrates.

Competitive reactions of styrene and *para*-substituted styrenes for the Hammett plot

MCPBA (0.03 mmol) was added to a mixture of styrene (0.02 mmol) and *para*(X)-substituted styrene (0.02 mmol, X = $-OCH_3$, $-CH_3$, –Cl, and –CN), cubane-type cobalt cluster **1** (0.001 mmol), and solvent (CH_3CN/CH_2Cl_2, 1 : 1 v/v; 1 mL). The mixture was stirred for 10 min at room temperature. The amounts of styrene before and after the reactions were measured by GC. The relative reactivities were determined using the following equation: $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$ where X_i and X_f are the initial and final concentrations of *para*-substituted styrenes and Y_i and Y_f are the initial and final concentrations of styrene.[12]

^{18}O-labeled $H_2{}^{18}O$ experiments

To a mixture of cyclohexene (0.005 mmol), cobalt catalyst (0.001 mmol), and $H_2{}^{18}O$ (10–40 μL, 0.556–2.22 mmol; 97% ^{18}O enriched, Aldrich Chemical Co.) in a dried solvent CH_3CN/CH_2Cl_2 (1 : 1 v/v; 1 mL) was added MCPBA (0.01 mmol). The reaction mixture was stirred for 3 min at room temperature and then directly analyzed by GC/mass analysis. The ^{16}O and ^{18}O compositions in cyclohexene oxide were determined by the relative abundance of mass peaks at $m/z = 97$ for ^{16}O and $m/z = 99$ for ^{18}O. All reactions were run at least three times and the average values are presented.

Analysis of the O–O bond cleavage products from the oxidation reactions of substrates by PPAA in the presence of the cubane-type cobalt(II) cluster 1

PPAA (0.04 mmol) was added to a mixture of substrate (0–0.16 mmol), cubane-type cobalt cluster **1** (0.001 mmol), and solvent (distilled CH_3CN/CH_2Cl_2, 1 : 1 v/v; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. Dodecane was used as an internal standard to quantify the yields of products and conversions of substrates. All reactions were run at least in triplicate, and the average conversions and product yields are presented. Conversions and product yields were calculated with respect to the substrate or PPAA.

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References

1 (*a*) B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457; (*b*) E. M. McGarrigle and D. G. Gilheany, *Chem. Rev.*, 2005, **105**, 1563; (*c*) S. V. Kryatov and E. V. Rybak-Akimova, *Chem. Rev.*, 2005, **105**, 2175; (*d*) M. Costas, M. P. Mehn, M. P. Jensen and L. Que Jr., *Chem. Rev.*, 2004, **104**, 939; (*e*) Z. Gross and H. G. Gray, *Adv. Synth. Catal.*, 2004, **346**, 165.

2 (*a*) W. Nam, *Acc. Chem. Res.*, 2007, **40**, 522; (*b*) D. Dolphin, T. G. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251; (*c*) C. Kim and Y. Watanabe, in *Encyclopedia of Catalysis*, Wiley, New York, 2002, pp. 593–643; (*d*) N. Jin, M. Ibrahim, T. G. Spiro and J. T. Groves, *J. Am. Chem. Soc.*, 2007, **129**, 12416; (*e*) D. E. Lansky and D. P. Goldberg, *Inorg. Chem.*, 2006, **45**, 5119; (*f*) G. Yin, J. M. McCoemick, M. Buchalova, A. M. Danby, K. Rodgers, V. W. Day, K. Smith, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, *Inorg. Chem.*, 2006, **45**, 8052; (*g*) M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Guler, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 948; (*h*) R. Zhang and M. Newcomb, *Acc. Chem. Res.*, 2008, **41**, 468; (*i*) M. E. Crestoni, S. Fornarini and F. Lanucara, *Chem. – Eur. J.*, 2009, **15**, 7863; (*j*) C. Mukherjee, A. Stammler, H. Bogge and T. Glaser, *Inorg. Chem.*, 2009, **48**, 9476.

3 (*a*) J. Rosenthal and D. G. Nocera, *Acc. Chem. Res.*, 2007, **40**, 543; (*b*) X. Zhang, K. Sasaki and C. L. Hill, *J. Am. Chem. Soc.*, 1996, **118**, 4809; (*c*) T. Punniyamurthy, S. S. J. Kalra and J. Iqbal, *Tetrahedron Lett.*, 1995, **36**, 8497; (*d*) D. Dhar, Y. Koltypin, A. Gedanken and S. Chandrasekaran, *Catal. Lett.*, 2003, **86**, 197; (*e*) I. Fernández, J. R. Pedro, A. L. Rosello, R. Ruiz, I. Castro, X. Ottenwaelder and Y. Journaux, *Eur. J. Org. Chem.*, 2001, 1235; (*f*) J. D. Koola and J. K. Kochi, *J. Org. Chem.*, 1987, **52**, 4545; (*g*) R. V. Patel, J. G. Panchal and S. K. Menon, *J. Inclusion Phenom. Macrocyclic Chem.*, 2010, **67**, 63; (*h*) W. Nam, I. Kim, Y. Kim and C. Kim, *Chem. Commun.*, 2001, 1262; (*i*) F. F. Pfaff, S. Kundu, M. Risch, S. Pandian, F. Heims, I. Pryjomska-Ray, P. Haack, R. Metzinger, E. Bill, H. Dau, P. Comba and K. Ray, *Angew. Chem.*, 2011, **123**, 1749, (*Angew. Chem., Int. Ed.*, 2011, **50**, 1711); (*j*) J. G. McAlpin, Y. Surendranath, M. Dinca, T. A. Stich, S. A. Stoian, W. H. Casey, D. G. Nocera and R. D. Britt, *J. Am. Chem. Soc.*, 2010, **132**, 6882; (*k*) B. K. Das and J. H. Clark, *Chem. Commun.*, 2000, 605; (*l*) P. Sarmah and B. K. Das, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 2014, **53**, 41; (*m*) A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Soc. Rev.*, 2013, **42**, 2262; (*n*) V. Artero and M. Fontecave, *Chem. Soc. Rev.*, 2013, **42**, 2338.

4 (*a*) T. J. Collins, S. Ozaki and T. G. Richmond, *J. Chem. Soc., Chem. Commun.*, 1987, 803; (*b*) W. Nam, J. Y. Ryu, I. Kim and C. Kim, *Tetrahedron Lett.*, 2002, **43**, 5487; (*c*) J. W. Shin, S. R. Rowthu, M. Y. Hyun, Y. J. Song, C. Kim, B. G. Kim and K. S. Min, *Dalton Trans.*, 2011, **40**, 5762.

5 (*a*) R. Chakrabarty, S. J. Bora and B. K. Das, *Inorg. Chem.*, 2007, **46**, 9450; (*b*) F. Evangelisti, R. Guttinger, R. More, S. Luber and G. R. Patzke, *J. Am. Chem. Soc.*, 2013, **135**, 18734; (*c*) R. Chakrabarty, B. K. Das and J. H. Clark, *Green Chem.*, 2007, **9**, 845; (*d*) C. E. Sumner Jr. and G. R. Steinmetz, *J. Am. Chem. Soc.*, 1985, **107**, 6124.

6 R. Chakrabarty, P. Sarmah, B. Saha, S. Chakravorty and B. K. Das, *Inorg. Chem.*, 2009, **48**, 6371.

7 R. Chakrabarty and B. K. Das, *J. Mol. Catal. A: Chem.*, 2004, **223**, 39.

8 D. Lee, L. Sorace, A. Caneschi and S. J. Lippard, *Inorg. Chem.*, 2001, **40**, 6774.

9 C. Hormillosa, S. Healy, T. Stephen and I. D. Brown, *Bond Valence Calculator, Version 2.0*, McMaster University, Canada, 1993, http://ccp14.ac.uk.

10 (*a*) P. King, R. Clérac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2004, 2670; (*b*) G. K.-Y. Ng, J. W. Ziller and A. S. Borovik, *Chem. Commun.*, 2012, **48**, 2546; (*c*) P. Mahata, S. Natarajan, P. Panissod and M. Drillon, *J. Am. Chem. Soc.*, 2009, **131**, 10140; (*d*) D. Lee,

P.-L. Hung, B. Singler and S. J. Lippard, *Inorg. Chem.*, 2002, **41**, 521.

11 P. A. Narayana, A. Mehra and P. Venkateswarlu, *Can. J. Phys.*, 1968, **46**, 325.

12 (*a*) S. H. Lee, J. H. Han, H. Kwak, S. J. Lee, E. Y. Lee, H. J. Kim, J. H. Lee, C. Bae, S. N. Lee, Y. Kim and C. Kim, *Chem. – Eur. J.*, 2007, **13**, 9393; (*b*) T. K. M. Shing, Y. Y. Yeung and P. L. Su, *Org. Lett.*, 2006, **8**, 3149; (*c*) R. A. Sheldon and J. K. Kochi, in *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981, ch. 2.

13 (*a*) G. Dubois, A. Murphy and T. D. P. Stack, *Org. Lett.*, 2003, **5**, 2469; (*b*) I. Garcia-Bosch, X. Ribas and M. Costas, *Adv. Synth. Catal.*, 2009, **351**, 348; (*c*) D. C. Duncan, R. C. Chambers, E. Hecht and C. L. Hill, *J. Am. Chem. Soc.*, 1995, **117**, 681; (*d*) J. P. Collman, Z. Wang, A. Straumanis and M. Quelquejeu, *J. Am. Chem. Soc.*, 1999, **121**, 460; (*e*) H. Tian, X. She, J. Xu and Y. Shi, *Org. Lett.*, 2001, **3**, 1929; (*f*) M. C. White, A. G. Doyle and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 7194; (*g*) X. Zuwei, Z. Ning, S. Yu and L. Kunlan, *Science*, 2001, **292**, 1139.

14 (*a*) D. E. De Vos, B. F. Sels, M. Reynaers, Y. V. Subba Rao and P. A. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 3221; (*b*) A. Murphy, G. Dubois and T. D. P. Stack, *J. Am. Chem. Soc.*, 2003, **125**, 5250; (*c*) C. Coperet, H. Adolfsson and K. B. Sharpless, *Chem. Commun.*, 1997, 1565; (*d*) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310; (*e*) A. Murphy, A. Pace and T. D. P. Stack, *Org. Lett.*, 2004, **6**, 3119; (*f*) A. Murphy and T. D. P. Stack, *J. Mol. Catal. A: Chem.*, 2006, **251**, 78; (*g*) S. Taktak, W. Ye, A. M. Herrera and E. V. Rybak-Akimova, *Inorg. Chem.*, 2007, **46**, 2929; (*h*) E. Hao, Z. Wang, L. Jiao and S. Wang, *Dalton Trans.*, 2010, **39**, 2660.

15 (*a*) Y. J. Song, M. Y. Hyun, J. H. Lee, H. G. Lee, J. H. Kim, S. P. Jang, J. Y. Noh, Y. Kim, S.-J. Kim, S. J. Lee and C. Kim, *Chem. – Eur. J.*, 2012, **18**, 6094; (*b*) Y. J. Song, S. H. Lee, H. M. Park, S. H. Kim, H. G. Goo, G. H. Eoom, J. H. Lee, M. S. Lah, Y. Kim, S.-J. Kim, J. E. Lee, H.-I. Lee and C. Kim, *Chem. – Eur. J.*, 2011, **17**, 7336.

16 S. H. Lee, L. Xu, B. K. Park, Y. V. Mironov, S. H. Kim, Y. J. Song, C. Kim, Y. Kim and S.-J. Kim, *Chem. – Eur. J.*, 2010, **16**, 4678.

17 (*a*) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1988, **110**, 8628; (*b*) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1987, **109**, 3812; (*c*) W. Adam, C. Mock-Knoblauch, C. R. Saha-Moller and M. Herderich, *J. Am. Chem. Soc.*, 2000, **122**, 9685; (*d*) C. Linde, M. Arnold, P.-O. Norrby and B. Akermark, *Angew. Chem.*, 1997, **109**, 1802, (*Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1723); (*e*) C. Linde, M. F. Anderlund and B. Akermark, *Tetrahedron Lett.*, 2005, **46**, 5597.

18 O. Bortolini and B. Meunier, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1967.

19 L. Garcia-Cosch, A. Company, X. Fontrodona, X. Ribas and M. Costas, *Org. Lett.*, 2008, **11**, 2095.

20 (*a*) J. T. Groves, J. Lee and S. S. Marla, *J. Am. Chem. Soc.*, 1997, **119**, 6269; (*b*) J. H. Han, S.-K. Yoo, J. S. Seo, S. J. Hong, S. K. Kim and C. Kim, *Dalton Trans.*, 2005, 402; (*c*) J. Bernadou and B. Meunier, *Chem. Commun.*, 1998, 2167; (*d*) W. Nam, M. H. Lim, S. K. Moon and C. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 10805; (*e*) G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, *Inorg. Chem.*, 2006, **45**, 3467; (*f*) W. Nam and J. S. Valentine, *J. Am. Chem. Soc.*, 1993, **115**, 1772; (*g*) S. H. Wang, B. S. Mandimutsira, R. Todd, B. Ramdhanie, J. P. Fox and D. P. Goldberg, *J. Am. Chem. Soc.*, 2004, **126**, 18.

21 (*a*) R. E. White, S. G. Sligar and M. J. Coon, *J. Biol. Chem.*, 1980, **255**, 11108; (*b*) T. G. Traylor, W. A. Lee and D. V. Stynes, *J. Am. Chem. Soc.*, 1984, **106**, 755; (*c*) T. G. Traylor, S. Tsuchiya, Y. S. Byun and C. Kim, *J. Am. Chem. Soc.*, 1993, **115**, 2775.

22 (*a*) M. Y. Hyun, S. H. Kim, Y. J. Song, H. G. Lee, Y. D. Jo, J. H. Kim, I. H. Hwang, J. Y. Noh, J. Kang and C. Kim, *J. Org. Chem.*, 2012, **77**, 7307; (*b*) M. Y. Hyun, Y. D. Jo, J. H. Lee, H. G. Lee, H. M. Park, I. H. Hwang, K. B. Kim, S. J. Lee and C. Kim, *Chem. – Eur. J.*, 2013, **19**, 1810; (*c*) N. Suzuki, T. Higuchi and T. Nagano, *J. Am. Chem. Soc.*, 2002, **124**, 9622; (*d*) J. T. Groves and Y. Watanabe, *Inorg. Chem.*, 1986, **25**, 4808.

23 (*a*) C.-J. F. Du, H. Hart and K.-K. D. Ng, *J. Org. Chem.*, 1986, **51**, 3162; (*b*) C.-T. Chen and J. S. Siegel, *J. Am. Chem. Soc.*, 1994, **116**, 5959; (*c*) A. Saednya and H. Hart, *Synthesis*, 1996, 1455.

24 Bruker AXS, *SMART Version 5.618 and SAINT Version 6.02a*, Madison, WI, USA, 2002.

25 G. M. Sheldrick, *Program Library for Structure Solution and Molecular Graphics: Version 6.2*, Bruker AXS, Madison, WI, 2000.