A Novel Dinuclear Ruthenium–1,8-Naphthyridine Catalyst for the Oxidation of Alcohols and the Epoxidation of Alkenes

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A novel ruthenium–1,8-naphthyridine complex is synthesized, characterized by X-ray analysis, and proven to be an active and stable catalyst in the oxidation of several alcoholic substrates and in the epoxidation of *trans-* and *cis*-stilbene and cyclooctene.

When an alcoholic group is part of a polyfunctional molecule or of a molecule that is sensitive towards acidic or alkaline reagents, the choice of effective and selective oxidants is rapidly narrowed.[1]. Accordingly, research leading to new mild and selective oxidation and epoxidation systems is still an important area. Several catalytic epoxidation systems are known using $RuCl_3$ with bipyridyl or substituted phenanthrolines.[2] In addition to mononuclear ruthenium polypyridyl complexes,[3] dinuclear complexes are also of interest as catalytic oxidants.[4] Oxo-bridged ruthenium dimers with 2,2′-bipyridyl ligands have received considerable attention as oxidants, due to their enhanced thermodynamic oxidation strength, which leads to accelerated rates of oxidation of organic compounds, or to oxidations that are otherwise unobservable with monomeric analogues.[4] However, due to their instability they have not been effective under catalytic conditions.[5]

In this study 1,8-naphthyridine (napy), a potentially dinucleating ligand of the carboxylate type,[6] is used as a ligand, bridging the two ruthenium centres thereby stabilizing the bridge already formed by chloride, oxygen or hydroxide.

The crystal structure of a novel dinuclear ruthenium(III) complex, $[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$ **1**, and its use as a catalyst for the oxidation of alcohols and for the epoxidation of alkenes is presented. The complex is highly soluble and catalytically active in the non-toxic solvent water, which provides for its facile recovery from organic reaction products by simple phase separation.

Compound **1** was synthesized from its chloride analogue,[‡] $[Ru_2(napy)_2Cl_4]$ **2**, by chloride replacement using an excess of $AgClO_4$ in acetone–water. $[Ru_2(napy)_2Cl_4]$ was in turn synthesized from commercial hydrated '$RuCl_3$' and naphthyridine in methanol.

X-Ray structure analysis[§] (Fig. 1) showed that the complex is a dinuclear Ru^{III}/Ru^{III} complex with the two naphthyridine ligands in a *trans* configuration. The bridging moieties consist of Cl^- and $OH^- \cdots H_2O$ ions, disordered over the crystallographic inversion centre in ratio 1 : 1.

The catalytic results are summarized in Tables 1 and 2.[¶] It is evident that the dinuclear complex is an active and stable catalyst for the oxidation of primary alcohols by $NaBrO_3$ (reaching from 520 for octanol up to 980 turnovers for *n*-butanol in 15 h) and for the oxidation of 1,2-cyclohexanediol yielding adipic acid (1000 turnovers in 15 h). Also secondary alcohols such as cyclohexanol and cyclobutanol are easily oxidized. Cyclobutanol is oxidized to cyclobutanone and propanoic acid, suggesting that both a two- and a one-electron oxidation step are present.[7]. The mononuclear complex *cis*-$[Ru(bpy)_2Cl_2]$[8] (which can be regarded as a mononuclear analogue for the dinuclear ruthenium complex) appears to be much less active under the same reaction conditions yielding only a small amount of cyclohexanemethanoic acid from cyclohexylmethanol; cyclohexanol proved to be not reactive at all, clearly showing the advantage of the dinuclear complex over the mononuclear complex. It is quite difficult to compare these results with alcohol oxidation data obtained with other complexes in the literature, because of the difference in substrates, co-oxidants, solvents and reaction conditions. However, some relevant literature examples are added to the data in Table 1. Complex **1** was also tested for its catalytic properties in the epoxidation of *trans-* and *cis*-stilbene and cyclooctene. Compared to the previously reported highly active catalyst $[RuO_2(bpy)\{IO_3(OH)_3\}](H_2O)_{1.5}$,[9] our complex is less selective when $NaIO_4$ is used as a co-oxidant. However, when dioxygen/butyraldehyde, a cheaper and a more environmentally acceptable co-oxidant, is used, much better reaction selectivities (up to 100% for 1,2-epoxycyclooctane), albeit with lower activities for the epoxidation reaction, were obtained. The mechanism of epoxidation is generally believed to proceed then by the autoxidation of butyraldehyde to peracids and alkylhydroperoxides, which can then be used as oxygen-transfer agents in the epoxidation of alkenes.[10]

The absorption spectrum of **1** in aqueous solution is characterized by a visible band at 394 nm which is characteristic of metal-to-ligand charge transfer (MLCT) d_{π}–p_{π}* transitions. A spectrophotometric titration[||] of **1** with Ce^{IV} in 0.1 mol dm^{-3}

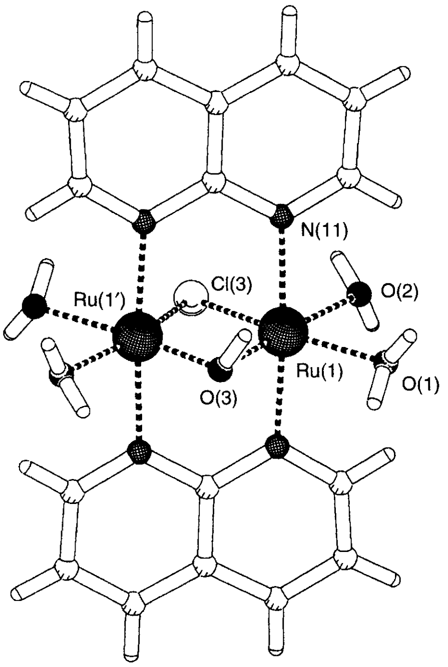

Fig. 1 Molecular structure of the dinuclear ruthenium complex **1**. Only one disorder component is shown. Hydrogen atoms and non- coordinated water molecules and perchlorate anions have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(1′) 2.4978(13), Ru(1)–O(1) 2.048(7), Ru(1)–O(2) 2.068(8), Ru(1)–O(3) 1.81(2), Ru(1)–Cl(3) 2.292(7), Ru(1)–N(11) 2.071(9), Cl(3)–Ru(1)–N(11) 87.7(3), O(3)–Ru(1)–N(11) 93.1(8), O(1)–Ru(1)–N(11) 88.2(3), O(2)–Ru(1)–N(11) 94.3(3), O(1)–Ru(1)–O(2) 83.5(3), O(3)–Ru(1)–Cl(3) 105.1(8). (Primed atoms related by symmetry operation −*x*, −*y*, −*z*.)

Table 1 Oxidation of alcoholic substrates, catalysed by $[Ru_2(napy)_2)OH)Cl(H_2O)_4][CLO_4]_4$ **1** and some reference compounds from the literature

Substrate	Reaction conditions	Turnovers (turnover h^{-1})	Product(s) (% Yield)
Cyclohexanol[a]	15 h (60 °C)	410 (27)	cyclohexanone (41)
Cyclohexanol[b]	2 h (room temp.)	62 (31)	cyclohexanone (75)[9]
Cyclohexanol[c]	15 h (60 °C)	0	
Octanol[a]	15 h (60 °C)	520 (35)	octanoic acid (52)
Cyclohexylmethanol[a]	15 h (60 °C)	950 (63)	cyclohexanemethanoic acid (95)
Cyclohexylmethanol[c]	15 h (60 °C)	210 (14)	cyclohexanemethanoic acid (21)
n-Butanol[a]	15 h (60 °C)	980 (65)	*n*-butanoic acid (74) propanoic acid (24)
1,2-Cyclohexanediol[a]	15 h (60 °C)	1000 (67)	adipic acid (100)
Benzylic alcohol[a]	4 h (60 °C)	910 (227)	benzoic acid (85) benzaldehyde (6)
Benzylic alcohol[d]	4 h (room temp.)	49 (12)	benzoic acid (72)[10]
Cyclobutanol[a]	15 h (room temp.)	990 (66)	cyclobutanone (44) propanoic acid (45)
Cyclobutanol[e]	4 h (room temp.)	81 (20)	cyclobutanone (100)[11]

Reaction conditions: [a] 0.3 mmol of substrate, 0.3 × 10^{-3} mmol catalyst and 0.6 mmol of $NaBrO_3$ as co-oxidant were mixed in 5 ml of water. [b] Catalyst *trans*-$[RuO_2(HIO_6)_2]^{6-}$ and $NaIO_4$ as co-oxidant.[11] [c] Catalyst *cis*-$[Ru(bpy)_2Cl_2]$ and $NaBrO_3$ as co-oxidant. [d] Catalyst $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ and $NaIO_4$ as co-oxidant.[9] [e] Catalyst $[Ru(dcbpy)_2(H_2O)_2]^{2+}$ [12] (electrochemically); dcbpy = 6,6′-dichlorobipyridine.

Table 2 Epoxidation of alkenes, catalysed by $[Ru_2(napy)_2(OH)Cl(H_2O)_4][ClO_4]_4$ **1** and some reference compounds from the literature

Substrate	Reaction conditions	Co-oxidant	Turnovers	Product(s) (% yield)
trans-Stilbene[a]	24 h (room temp.)	$NaIO_4$	760	benzaldehyde (62) benzoic acid (10) *trans*-stilbene oxide (4)
trans-Stilbene[b,c]	72 h (40 °C)	O_2/isobutyraldehyde	980	benzaldehyde (15) *trans*-stilbene oxide (83)
cis-Stilbene[b,c]	72 h (40 °C)	O_2/isobutyraldehyde	660	benzaldehyde (13) *cis*-stilbene oxide (53)
trans-Stilbene[d]	15 h (room temp.)	$NaIO_4$	249	*trans*-stilbene oxide (99)[10]
cis-Stilbene[d]	15 h (room temp.)	$NaIO_4$	189	*cis*-stilbene oxide (75)[10]
Cyclooctene[b,c]	48 h (40 °C)	O_2/isobutyraldehyde	840	1,2-epoxycyclooctane (84)

Reaction conditions: [a] 0.15 mmol of *trans*-stilbene, 0.15 × 10^{-3} mmol catalyst and 0.3 mmol of $NaBrO_3$ or $NaIO_4$ were dissolved in a mixture of 2 ml of water and 2 ml of 1,2-dichloroethane. [b] 0.15 mmol of *trans*-stilbene, 54 µl isobutyraldehyde and 0.15 10^{-3} mmol catalyst were dissolved in a vigorously stirred aerated mixture of 2 ml of water and 2 ml of 1,2-dichloroethane. [c] Blank experiments without the ruthenium catalyst yielded no more than 10% conversion under the same reaction conditions. [d] Catalyst $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot1.5H_2O$.[9]

CF_3SO_3H shows a two-electron oxidation of $[Ru^{III}Ru^{III}(napy)_2(H_2O)_4Cl(OH)]^{4+}$ to the $Ru^{IV}Ru^{IV}$ analogue, with an isobestic point at 390 nm. A plot of the absorbance of **1** at 384 nm (also observed at other wavelengths) *vs*. the Ce : [Ru_2] mol ratio is linear (R^2 = 0.987), with an apparent end point at Ce : [Ru_2] mol ratio of 2 ± 0.2. Addition of an excess of $NaBrO_3$ to the $Ru^{III}Ru^{III}$ species gives a similar absorbance spectrum (as of the high-valent complex obtained with cerium), albeit at a slower rate. The spectroscopic and oxidation results suggest that the $Ru^{III}Ru^{III}$ couplex is oxidized to $Ru^{IV}Ru^{IV}$ by $NaBrO_3$, after which this high-valent species can react either by two subsequent one-electron steps or by a two-electron step back to $Ru^{III}Ru^{III}$, thereby oxidizing alcoholic substrates. However, more detailed (electrochemical) experiments are needed to support this mechanism. In addition, we are currently investigating the catalytic potential of ruthenium complexes with 1,8-naphthyridine derivatives.

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Footnotes

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‡ *Selected data* for **1**: ^1H NMR (300 MHz, 0.1 mol dm^{-3} CF_3SO_3D *vs*. 4,4-dimethyl-4-silapentanesulfonic acid), δ 7.83 (dd, 4H, $H^{3,6}$), 8.57 (dd, 4H, $H^{4,5}$), 8.90 (dd, 4H, $H^{2,7}$). For **2**: ^1H NMR [300 MHz, $(CD_3)_2SO$ *vs*. $SiMe_4$), δ 7.76 (m, 4H, $H^{3,6}$), 8.48 (dd, 4H, $H^{4,5}$), 9.53 (dd, 4H, $H^{2,7}$). Elemental analysis. Calc. for $C_{16}H_{12}Cl_4N_4Ru_2\cdot2H_2O$: C, 30.02; H, 2.52; Cl, 22.15; N, 8.75. Found: C, 29.94; H, 2.53; Cl, 22.91; N, 7.95%.

§ *Crystal data* for compound **1**, $C_{16}H_{21}Cl_5N_4O_{21}Ru_2\cdot3H_2O$, M_r = 1038.81, green, needle-shaped crystal (0.05 × 0.10 × 0.60 mm), triclinic, space group $P\bar{1}$ (no. 2) with a = 8.7920(9), b = 10.2100(12), c = 11.0160(12) Å, α = 111.089(11), β = 109.759(9), γ = 100.608(9)°, U = 813.98(17) Å^3, Z = 1, D_c = 2.119 g cm^{-3}, $F(000)$ = 516, µ(Mo-Kα) = 14.4 cm^{-1}, 5356 reflections measured, 3737 independent, R_{int} = 0.100, (2.21° < θ < 27.49°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD4 Turbo diffractometer on rotating anode. Data were corrected for *Lp* effects and for a linear decay of 4% of the reference reflections, but not for absorption. The structure was solved by automated Patterson methods (SHELXS86). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement. Refinement converged at a final $wR2$ value of 0.191, $R1 = 0.082$ [for 2298 reflections with $F_O > 4\sigma(F_O)$], $S = 1.01$, for 266 parameters. A final difference Fourier map showed no residual density outside -1.32 and 1.48 e Å^{-3} (near Ru). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ All catalytic reactions were conducted under oxygen. Specific blank experiments did not show any activity towards the substrate unless stated otherwise. All reaction substrates, except adipic acid, were analysed by gas chromatography and satisfactory compared to commercial samples. Adipic acid was analysed by ^{1}H NMR.

|| Spectrophotometric redox titrations were carried out by adding aliquots of a 1.8×10^{-3} mol dm^{-3} solution of Ce^{IV} in 0.1 mol dm^{-3} CF_3SO_3H to aliquots (0.5 ml) of a 3.1×10^{-4} mol dm^{-3} solution of **1** in 0.1 mol dm^{-3} CF_3SO_3H. The volume was adjusted to 3 ml by addition of 0.1 mol dm^{-3} CF_3SO_3H, and the changes were monitored in the range 200–600 nm. The Ce : [Ru$_2$] mol ratio was varied from 0 to 6. Ce^{IV} solutions in 0.1 mol dm^{-3} CF_3SO_3H were prepared from $[NH_4]_2[Ce(NO_3)_6]$.

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