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Ruthenium complexes with naphthyridine ligands. Synthesis, characterization and catalytic activity in oxidation reactions †

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New ruthenium complexes with 1,8-naphthyridine (napy) or derivatives thereof as ligands have been prepared and characterized. Three groups of complexes were obtained. The first consists of three dinuclear ruthenium complexes with two ligands (1,8-naphthyridine and pyridopyrazine) co-ordinated to two ruthenium ions in a bridging fashion. The second consists of two ruthenium dinuclear complexes having one ligand (2,7-dimethoxy- or 2,7-dichloro-1,8-naphthyridine, abbreviated to dmnapy and dcnapy respectively) co-ordinated to two ruthenium atoms. Proton NMR spectra for both complexes in aqueous solution and in acetonitrile revealed the conversion of a symmetrical form, suggesting dinucleating behaviour of the ligand, into an asymmetrical form, suggesting mononucleating behaviour of the ligand. The third group consists of a mono- and a di-nuclear complex with the ligand 2,7-di(phenylazo)-1,8-naphthyridine. The catalytic activity of the novel naphthyridine complexes in oxidation reactions has been studied. The catalytic oxidation of alcohols and the epoxidation of *trans*-stilbene were examined and the different reaction rates and selectivities are discussed in a comparative way. The active high-valent species resulting from the $[Ru_2(napy)_2(H_2O)_4Cl(OH)]^{4+}$ complex is discussed in more detail.

When an alcoholic group is part of a polyfunctional molecule or a molecule that is sensitive towards acidic or basic reagents the choice of effective and selective oxidants is rapidly narrowed.[1] Therefore, research leading to new mild and selective oxidation systems is an important area. In addition to mononuclear ruthenium polypyridyl complexes,[2] dinuclear complexes are of major interest as catalytic oxidants.[3]

Dinuclear ruthenium complexes of the type $[\{Ru(H_2O)L_2\}_2O]$, where L is 2,2′-bipyridine (bpy) or a ring-substituted analogue, display unique catalytic capabilities for water oxidation, both electrochemically and in reactions with strong oxidants in homogeneous solution.[4–6] These reactions have considerable intrinsic interest, *e.g.* in understanding how redox metal clusters can overcome kinetic barriers imposed by reactant non-complementarity.[3] The presence of two ruthenium centres with aqua ligands and multiple redox states with potentials suitable for oxygen evolution makes these complexes attractive candidates for water oxidation. Besides being of interest for the oxidation of water, these ruthenium dimers are also potential catalysts for oxidation of organic substrates.[7]

The $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ dimer has especially received increasing attention as an oxidation catalyst in this respect.[2–7] This dinuclear complex has been shown to be an effective oxidant towards a variety of organic substrates, at least after being electrochemically oxidized to the $Ru^{IV}Ru^{V}$ oxidation state. The enhanced thermodynamic oxidizing strength of the $Ru^{IV}Ru^{V}$ dinuclear complex leads to accelerated rates of oxidation of a series of organic substrates, when compared to the monomeric analog $[Ru^{IV}O(bpy)_2(py)]^{2+}$ (py = pyridine). The extent of the rate enhancement is substrate dependent, *i.e.* 300 times as fast for certain alcohols, 60 times for ethanol and 40 times for olefins.[7] Quantitative catalytic conversion of organic substrates, however, cannot be performed with this complex because of its instability. Although the dinuclear ruthenium cation $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ is stable in basic solution, its high-oxidation-state forms, $Ru^{III}Ru^{IV}$ and $Ru^{IV}Ru^{V}$, are unstable at high pH, undergoing self-reduction by oxidation of ligands.[8] Under acidic conditions the dimer is known to undergo reductive cleavage of the $Ru^{III}{}_2$ form leading to the formation[3] of two molecules of *cis*-$[Ru(H_2O)_2(bpy)_2]^{2+}$. Our aim has been to synthesize dinuclear complexes with a ligand that bridges the two ruthenium centres, thereby improving the stability of the dinuclear complex, and further constraining the steric effects.

1,8-Naphthyridine (napy) and derivatives have been studied before as ligands forming di-[9] and mono-nuclear complexes.[10,11] Interest in these ligands arose from the desire to study the unusual manifestations caused by the formation of four-membered chelate rings when the two nitrogen sites bind to one central metal. The result was the characterization of complexes with abnormally high co-ordination numbers, which are favoured as a result of the small 'bite' of 2.2 Å for the 1,8-naphthyridine ligands. An example of this kind of co-ordination behaviour[11] is the complex $[Ru(napy)_4]^{2+}$. The ligand has also been reported[9] to be able to form dinuclear complexes with the general formula $[M_2(\mu\text{-napy})_2(\mu\text{-X})_2Y_2]$, where M is Cu^{II} and X and Y are Cl^- or CO_3^-, or $[M_2(\mu\text{-napy})_4]^{n+}$, where M is Fe^{II}, Cd^{II} or Hg^{II}. Therefore, napy, with a basicity nearly equivalent to that of pyridine, can be considered to be both a potentially dinucleating ligand of the carboxylate type and a mononucleating ligand.

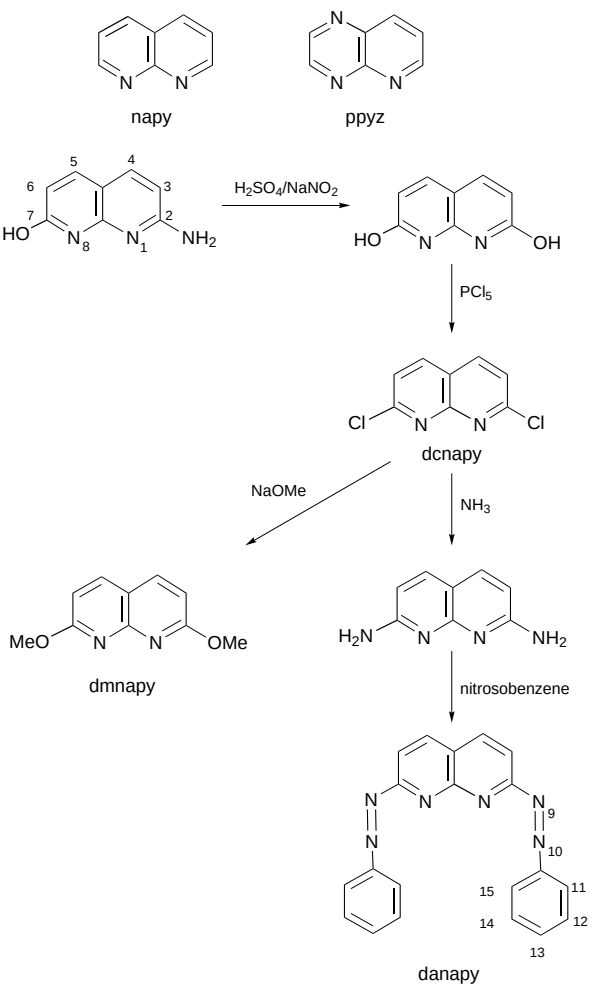
We previously communicated[12] the synthesis, crystal structure and preliminary catalytic reactivity of a dinuclear ruthenium(III) complex with 1,8-naphthyridine, $[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$ **2**. In this paper the syntheses and full characterization (NMR, Fourier-transform IR, UV/VIS spectroscopy and elemental analysis) of this and several other novel ruthenium complexes of napy derivatives which contain electron-withdrawing or -donating groups are described. The performance of these complexes as oxidation catalysts is investigated, and the different reactions are discussed in a comparative way. The active high-valent species resulting from the $[Ru_2(napy)_2(H_2O)_4Cl(OH)]^{4+}$ complex is discussed in significant detail.

Results and Discussion

Synthesis of the ligands

The synthesis of 2,7-dichloro-1,8-naphthyridine followed the same general procedure reported earlier by Newkome *et al.*[13]

† *Supplementary data available* (No. SUP 57294, 3 pp.): elemental analyses and IR data. See *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1.



Scheme 1

It began with the preparation of 2-amino-7-hydroxy-1,8-naphthyridine (see Scheme 1); this material was converted into its diazonium salt which was hydrolysed to form the desired 2,7-dihydroxy-1,8-naphthyridine. Our procedure differs from Newkome's in this step only in the work-up and recovery of the product. Conversion of the hydroxy groups into the desired 2,7-dichloro-1,8-naphthyridine using a mixture of phosphorus pentachloride and phosphorus trichloride oxide worked well, even when the procedure was scaled up to twenty-fold over the original report.[13] The intermediates and the final product were easily identified by their ^{1}H NMR spectra; the unsymmetrical shifts of the 2-amino-7-hydroxy at δ 7.76 ($H^{4,5}$), 6.46 (H^6) and 6.22 (H^3) were converted into the two symmetrical doublets (δ 7.78 and 6.38) for the dihydroxy compound. Conversion into the dichloro derivative caused these two doublets to shift to δ 8.15 and 7.61. The synthesis of the dimethoxy derivative was accomplished by refluxing a suspension of the dichloro derivative with an excess of sodium methoxide in dry methanol. The spectrum of the isolated product showed resonances for the aromatic protons at δ 8.21 and 6.94, together with a large singlet at δ 4.01 for the methoxy protons.

2,7-Di(phenylazo)-1,8-naphthyridine is accessible in two steps from the readily prepared 2,7-dichloro-1,8-naphthyridine.[13] Reaction of the dichloro compound with ammonia gas in phenol at 170 °C for 20 h was carried out as described by Collin and Youinou[14] and yielded 2,7-diamino-1,8-naphthyridine, albeit in significantly lower yield (20 *versus* 94%) than reported by these authors. Part of the difficulty may originate from the need of keeping a sufficiently high concentration of ammonia in the reaction vessel. 2,7-Diamino-1,8-naphthyridine was treated with nitrosobenzene as described by Collin and Youinou, although our conditions were somewhat more drastic. Chromatography of the product on neutral alumina yielded 2,7-di(phenylazo)-1,8-naphthyridine as an orange powder in 22% yield from the diamino starting material.

Synthesis and characterization of the ruthenium complexes

The syntheses of the ruthenium complexes were performed in a straightforward way, although some problems were encountered. In general the choice of reaction solvent proved to be quite important for the ultimate purity of the complexes. Ruthenium complexes with the ligands napy, ppyz and danapy were prepared in methanol. Earlier attempts to perform the complex syntheses in dimethylformamide instead of methanol yielded irreproducible results or products that contain carbon monoxide (CO co-ordinated to Ru, IR bands 1790 cm^{-1} for the napy derivative and 1820 cm^{-1} for the ppyz derivative). Elemental analyses of all complexes proved to be satisfactory and are summarized in SUP 57294.

The ^{1}H NMR spectra of the complexes are characterized by deshielding of the aromatic protons relative to the free heterocycle. This change in the proton environment upon co-ordination results from a decrease in electron density induced by the positive ruthenium centre. Proton NMR data for the complexes with napy and ppyz prepared in methanol showed that highly symmetrical compounds were formed. For both complexes only one set of ligand signals (two doublets and a triplet for the napy complex, and five signals for the ppyz complex) was found in the ^{1}H NMR spectra. Elemental analyses agree with ruthenium complexes in which the atom ratios are in accordance with $Ru_2(napy)_2Cl_4$ **1** and $Ru_2(ppyz)_2(dmso)_2Cl_4$ **3** (dmso = dimethyl sulfoxide).

With the ligand danapy two different ruthenium complexes could be obtained. After refluxing the ligand and $RuCl_3(H_2O)_3$ in methanol a red complex precipitated which showed an asymmetrical ^{1}H NMR spectrum with an integral of 14 protons. Elemental analysis indicates that a mononuclear complex, $Ru(danapy)Cl_2$ **6**, was formed. The inequivalence of the H^3, H^4, H^5 and H^6 protons in the NMR spectrum suggests that the ruthenium atom co-ordinates to N^1 or N^8 of the naphthyridine unit and one nitrogen of the azo-group (N^{10}). If the ruthenium co-ordinated to the two nitrogens of the naphthyridine one would expect the equivalence of H^3 and H^6 and H^4 and H^5. From the reaction filtrate a green complex could be isolated, yielding also an asymmetric NMR spectrum, however with an elemental analysis indicative for a complex with the ratio of elements as in $Ru_2(danapy)Cl_6$ **7**. In this case no reduction to Ru^{II} had occurred.

When dcnapy and $RuCl_3(H_2O)_3$ were refluxed in methanol two different complexes were formed in solution: a symmetrical complex showing only two doublets at δ 8.49 and 7.76, and a compound showing four doublets at δ 8.15, 8.06, 7.40 and 6.78 in the ^{1}H NMR spectrum indicating lower symmetry. The latter spectrum is characteristic of complexes wherein napy acts as a monodentate ligand.[11,15] The ratio of the asymmetric to the symmetric complex was changed with reaction conditions. The amount of asymmetric complex increased with longer reaction times, while that of the symmetric complex could be enhanced by increasing the ionic strength (*i.e.* addition of lithium chloride) of the reaction solution. When the reaction was performed in aqueous solution without LiCl only the asymmetric complex was formed. Precipitation of the asymmetric compound, or a mixture of asymmetric and symmetric complexes, was troublesome due to their hygroscopic properties. However, if the co-ordination reaction of dcnapy was carried out in ethyl acetate only the symmetric product was formed which could be isolated by filtration. Elemental analysis indicates that the formed complex has a ratio of elements as in $Ru_2(dcnapy)Cl_4$ **5**. The existence of a polymeric chain cannot be excluded. The fact that only one dcnapy ligand is co-ordinated to two ruthenium atoms must be due to steric constraints preventing

Table 1 Electronic absorption spectral data at 298 K of the ruthenium complexes

Complex	Solvent	λ_{max}/nm (ε/M^{-1} cm^{-1})
$Ru_2(napy)_2Cl_4(H_2O)_2$	dmso	438 (3610), 270 (7610)
$[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4\cdot 3H_2O$	Water	393 (9651), 305 (10 968), 258 (24 379)
	MeCN	368 (11 342), 313 (9993), 242 (19 573)
$Ru_2(ppyz)_2(dmso)_2Cl_4(H_2O)_3$	dmso	492 (10 930), 323 (12 420), 276 (16 510)
$Ru_2(dmnapy)Cl_4$	MeOH	399 (16 651), 323 (34 341)
	MeCN*	415 (14 210), 319 (16 210)
$Ru_2(dcnapy)Cl_4$	MeOH	389 (13 844), 320 (30 271), 312 (25 339)
	MeCN	416 (8121), 319 (7212), 311 (6563)
$Ru_2(danapy)Cl_6(H_2O)_4$	Water	612 (5340), 396 (15 720), 332 (13 810), 297 (8140)
	MeCN	604 (4060), 397 (14 310), 329 (11 520), 315 (10 800)
$Ru(danapy)Cl_2(H_2O)_2$	Water	385 (23 000), 318 (26 200), 308 (17 500)
	MeCN	547 (4600), 385 (12 420), 326 (11 030)

* After equilibration in acetonitrile at room temperature for 2 weeks.

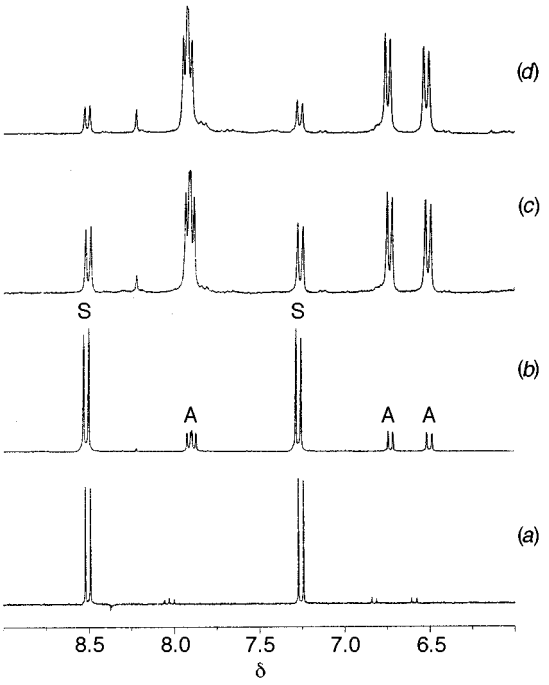


Fig. 1 Proton NMR spectra of the aromatic region of the dmnapy complex **4** in D_2O (4.5 mM) showing the conversion of the symmetric complex into the asymmetric complex: (*a*) starting solution; (*b*) after 24 h at 80 °C; (*c*) after 48 h at 80 °C; (*d*) after 72 h at 80 °C

fitting of two chloride (*trans* oriented) groups of each dcnapy ligand around the Ru^{II}. However, two such ligands in a *cis* orientation would be possible.

The results with the ligand dmnapy are very similar to those with dcnapy. Also with this ligand a mixture of both an asymmetric and a symmetric complex is obtained in methanol or water and also here only the symmetric compound is isolated when the synthesis is done in ethyl acetate (^{1}H NMR spectroscopy shows two doublets and a singlet at δ 8.50, 7.25 and 4.23, respectively). Elemental analysis agrees with a dinuclear or polymeric complex with the atom ratio $Ru_2(dmnapy)Cl_4$ **4**.

The symmetric complexes obtained in ethyl acetate can be converted into asymmetric complexes by heating in aqueous solution. For the dmnapy complex this is illustrated in Fig. 1. The symmetric complex **4** (obtained in ethyl acetate) was dissolved in D_2O (4.5 mM) and heated at 80 °C for 3 d. Each day a ^{1}H NMR spectrum was taken and the spectra clearly show the clean conversion of the symmetric complex (two doublets) into an asymmetric complex (four doublets of which two are overlapping). In the aliphatic region the intensity of the singlet signal of the CH_3 was also doubled (not shown in this figure). A difference between the dmnapy and dcnapy complexes appears to be the rate of conversion into the asymmetric isomer. The conversion of the dcnapy complex is much faster (5 h for complete conversion) than that of the dmnapy complex (3 d for complete conversion) in D_2O at 80 °C. The exact structural formula for the asymmetric complexes could not be determined because of problems with isolation as described above. Comparison of the NMR data with literature results,[11,15] however, suggests that the naphthyridine derivatives change from di- to mono-nucleating ligands.

Although attempts were made to prepare the aquated derivatives of complexes **1** to **7**, the only reproducible result could be obtained for the $Ru_2(napy)_2Cl_4$ complex. The complex $Ru_2(napy)_2Cl_4$ was converted into its aquated derivative, $[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4\cdot 3H_2O$ **2** by refluxing in acetone–water with an excess of $AgClO_4$. The resulting complex shows only three signals in the ^{1}H NMR spectrum (two doublets and a triplet, at δ 8.92, 8.56 and 7.81, respectively) indicating the existence of a highly symmetric complex. Crystals suitable for X-ray analysis were obtained and the structure briefly communicated before [12] (for schematic structure see Scheme 2 upper left corner). The structure proves the dinuclearity of the complex and explains the high symmetry as observed in the NMR spectrum. Attempts to convert the other complexes into their aquated forms have failed so far.

Electronic spectra

Staniewicz and Hendricker [11] discussed the synthesis and spectroscopic properties of a mononuclear tetrakis ruthenium(II) complex with 1,8-naphthyridine, $[Ru(napy)_4][PF_6]_2$. They concluded that its ground state has significant charge-transfer character and, therefore, metal-to-ligand π bonding contributes to the stability of the complex. The considerably anodic potentials of the complex demonstrated the ability of napy to participate in π-back bonding, and thereby stabilize the ruthenium(II) state in the tris(2,7-dimethyl-1,8-naphthyridine) complex. They also concluded that the mononuclear $[Ru(napy)_4]^{2+}$ complex undergoes solvolysis upon dissolution in MeCN with a corresponding change from red to yellow, indicative of a shift in the metal-to-ligand charge-transfer (MLCT) band. The replacement of napy by MeCN apparently stabilizes the t_{2g} level of Ru^{II}, thereby causing the energy of the d $Ru^{II} \rightarrow \pi^*$ (napy) transition to move to higher energy.

Table 1 presents the visible and UV maxima for the new ruthenium complexes. The visible bands for the complexes described in this paper exhibit high molar absorption and are assigned as t_{2g}–π^* MLCT transitions in analogy with those of previous ruthenium complexes with 1,8-naphthyridine ligands.[9,10] The spectra of the ruthenium complexes also display intraligand bands in the UV region, which are shifted compared to the bands of the free heterocycles. The complexes $Ru_2(napy)_2Cl_4$ and $Ru_2(ppyz)_2(dmso)_2Cl_4$ were not soluble in any other solvent than dmso and therefore the solvolysis by acetonitrile could not be studied. The MLCT band of [Ru-

$(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$ at 393 nm shifts upon dissolution in acetonitrile to 368 nm, suggesting water replacement by acetonitrile. The MLCT band of $Ru_2(dmnapy)Cl_4$, 399 nm in methanol, shifts to 415 nm upon dissolution in acetonitrile which would indicate replacement of ligands, or chloride, by acetonitrile. However, this solvolysis occurs in two steps. Upon dissolution in acetonitrile a new band appears in the spectrum at 604 nm apart from the MLCT shift. After standing in acetonitrile for extended time (1–2 weeks, room temperature) the band at 604 nm disappears, while the MLCT band does not change. The ^1H NMR spectrum of $Ru_2(dmnapy)Cl_4$ in CD_3CN shows the slow conversion of the symmetric complex into the asymmetric complex, already described before when water is used as the solvent. Dissolution of $Ru_2(dcnapy)Cl_4$ in acetonitrile shifts the MLCT band at 389 to 416 nm and has a large decreasing effect on the intensity of all bands in the spectrum, indicating acetonitrile co-ordination. The ^1H NMR spectrum of $Ru_2(dcnapy)Cl_4$ in CD_3CN shows a fast conversion of the symmetric complex into the asymmetric complex (50% conversion within 2 min). The conversions of the symmetric into the asymmetric compounds are significantly faster in acetonitrile than in water, showing the stronger co-ordination properties of acetonitrile. The observed bathochromic shift instead of the usual hypsochromic shift for both compounds suggests that the acetonitrile co-ordination destablilizes the ruthenium(II) state compared to the original complex.

The spectrum of $Ru(danapy)Cl_2$ in acetonitrile shows an additional band at 547 nm compared to the spectrum obtained in water. The original MLCT band of the complex at 385 nm is not affected by dissolution in acetonitrile. The visible spectrum of the dinuclear complex with the danapy ligand, $Ru_2(danapy)Cl_6$, does not seem to be affected upon dissolution of the complex in acetonitrile. In fact, only a small red shift for the intraligand band at 297 nm is observed.

Infrared spectroscopy

Fourier-transform infrared spectra (4000–200 cm^{-1}) were obtained for all complexes and ligands. In SUP 57294 only the characteristic bands which change substantially upon complexation are listed. Absorptions due to napy from 1600 to 650 cm^{-1} have been previously assigned, while those below 650 cm^{-1} have been attributed to ligand deformations.[16] As reported before, the change in the position of the skeletal modes of free napy (1558, 1228, 1105 and 760 cm^{-1}) with respect to the complexes indicates co-ordination.[9,10] This was the case for all novel complexes and no evidence of non-co-ordinated ligands was found in any of the spectra of the complexes. In the spectrum of $Ru_2(ppyz)_2(dmso)_2Cl_4$ the frequencies at 1019 and 953 cm^{-1} originate from co-ordinated dmso, as the infrared spectrum of the crude complex of ruthenium with ppyz before recrystallizing from dmso does not show these frequencies. Bonding of dmso through the sulfur usually causes[17] an increase in ν_{SO} to about 1100 cm^{-1} (from 1055 cm^{-1} for free dmso), whereas a shift to the lower range of 1000–900 cm^{-1} is indicative of co-ordination by oxygen.[18] Therefore, the dmso in this complex appears to be bound through the oxygen atom. For all complexes distinct absorbances in the far-infrared region were also observed compared to the unco-ordinated ligands. However, the assignment of these frequencies to metal–ligand interactions (Ru–Cl, Ru–N) by comparison of the spectra of the unco-ordinated ligands and the ruthenium complexes is difficult. This is due to the fact that complex formation may activate ligand vibrations which are inactive in the free state, and that Ru–Cl and Ru–N vibrations occur in the same infrared region.

Staniewicz *et al.*[19] have reported a low-frequency infrared study on $[Ru(napy)_4][PF_6]_2$ and could assign four distinct bands (315, 293, 255 and 227 cm^{-1}) to Ru–N stretching modes, by comparing the infrared spectrum of free napy and that of the ruthenium complex. The low-frequency spectra of $Ru_2(napy)_2Cl_4$ and $[Ru_2(napy)(H_2O)_4Cl(OH)][ClO_4]_4$ also display new absorptions compared to free napy in this region. The spectrum of $Ru_2(napy)_2Cl_4$ shows four intense bands at 339, 306, 261 and 250 cm^{-1}, which can be attributed to both Ru–N or Ru–Cl stretches (ν_{Ru-Cl} are usually found[20] between 280 and 350 cm^{-1}). Also five distinct absorbances are found for $[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$ in the far-infrared region [albeit much weaker than in the spectrum of $Ru_2(napy)_2Cl_4$], at 224, 247, 253, 279 (which might be assigned to Ru–N stretches) and 357 cm^{-1} (which might originate from Ru–Cl–Ru stretch), respectively. To exclude displacement of the aqua groups by iodide, the IR spectrum was also obtained in a polyethylene pellet; this did not alter the already observed frequencies in CsI.

Krause and Krause[21] assigned the Ru–N and Ru–Cl vibrations of several isomers of the ruthenium complexes with the ligand 2-(phenylazo)pyridine (azpy), $Ru(azpy)_2Cl_2$. Bands at 308 and 336 cm^{-1} were assigned to Ru–Cl stretching modes, bands around 280, 304 and 376 cm^{-1} to Ru–N (azo) modes and bands around 268 and 358 cm^{-1} to Ru–N (pyridine) modes. The IR spectrum of $Ru_2(danapy)Cl_6$ displays bands at 327 and 318 cm^{-1}, which might be Ru–Cl modes, and a weak band at 269 cm^{-1}, which might be tentatively assigned to a Ru–N (pyridine) mode. The mononuclear complex $Ru(danapy)Cl_2$ shows a very broad absorption at 322 cm^{-1}, which could comprise and include several stretching modes, and a weak absorption at 254 cm^{-1}, which might be a Ru–N (pyridine) mode.

Cyclic voltammetry

The reduction potentials, Ru^{III}–Ru^{II}, of ruthenium complexes are known to depend on the presence of back-bonding ligands in the co-ordination sphere with the potential increasing as the number of such ligands is increased.[22] Qualitatively, this change of potential can be attributed to a stabilization of the ruthenium(II) t_{2g} level by increased back bonding, whereas π bonding between ruthenium(III) and pyridine-type ligands is thought to be insignificant.[23] On varying the ligand environment surrounding the Ru^{II} the potential of the couple changes, thus yielding information about the relative π interaction between the metal and ligand.

The π-accepting properties of the naphthyridine ligand may be manipulated by adding substituents to the naphthyridine rings. It was expected that the π-accepting properties of these ligands would increase in the order dmnapy < napy < dcnapy < danapy.[24]

Unfortunately, it was impossible to obtain cyclic voltammograms of $Ru_2(napy)_2Cl_4$ and $Ru_2(ppyz)_2(dmso)_2Cl_2$ in acetonitrile due to their poor solubility. Attempts to measure the electrochemical response in other solvents like water, dmso and mixed solvents did not give satisfactory results. The ruthenium complexes with dmnapy, dcnapy and the mononuclear complex with danapy all gave an irreversible oxidation wave at +0.98 V *vs.* Ag–AgCl in acetonitrile–tetrabutylammonium hexafluorophosphate solution which can be attributed to chloride oxidation.[25] The complex $Ru_2(danapy)Cl_6$ did not show any electrochemical response in acetonitrile or water. The dcnapy complex showed an additional oxidation wave at 1.26 V *vs.* Ag–AgCl with a peak separation of 60–70 mV, depending on the scan rate, indicating a (quasi) reversible one-electron transfer (Fig. 2). The complex $Ru_2(dmnapy)Cl_4$ did not seem to give this additional response in acetonitrile at first sight; however, after prolonged standing at room temperature of the solution an additional wave was observed at 1.28 V *vs.* Ag–AgCl with a peak separation of 60–70 mV. As discussed above, NMR spectroscopy had shown that in acetonitrile the symmetrical dcnapy complex was immediately converted into the asymmetrical complex, whereas the symmetric dmnapy complex only slowly converts into the asymmetric compound. The observed electrochemical responses around 1.25 V there-

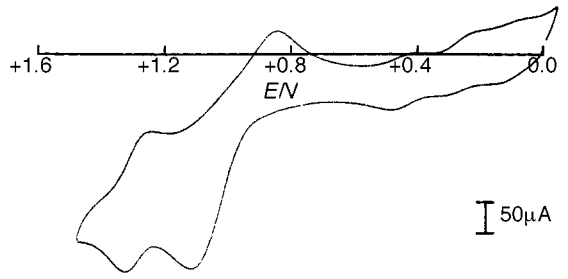
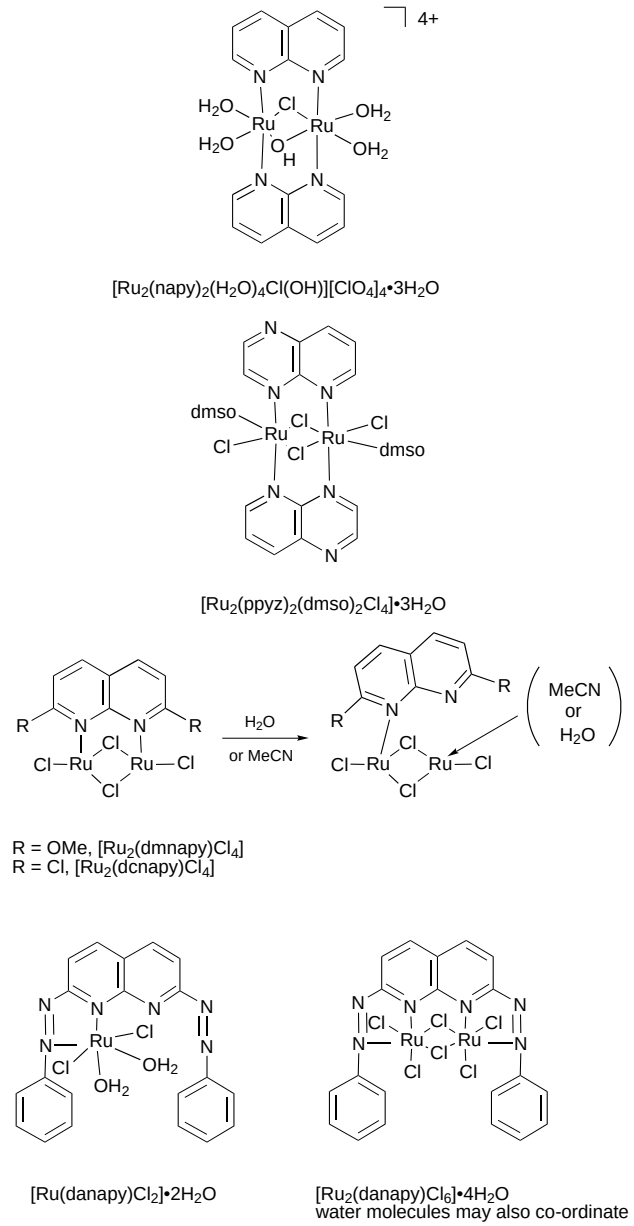


Fig. 2 Cyclic voltammogram of $Ru_2(dcnapy)Cl_4$ (1.5×10^{-3} M) in $MeCN–NBu_4ClO_4$ solution (platinum working electrode, Ag–AgCl reference electrode, scan rate 100 mV s^{-1}



Scheme 2

fore seem to originate from the secondary asymmetric complexes.

In aqueous solution an electrochemical response for the complex $[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$ could be obtained. However, this response appeared to be strongly influenced by adsorption phenomena on the electrode. Variation in solvent (phosphate, triflate, acetate buffer, acetonitrile), or electrodes (platinum, glassy carbon) did not solve this problem. Meyer and co-workers [3a] addressed the same phenomena discussing the electrochemical irreversible response of the bpy dimer in 0.1 M $HClO_4$. They suggested that this irreversibility arises because of the precipitation of the dimer onto the electrode surface.

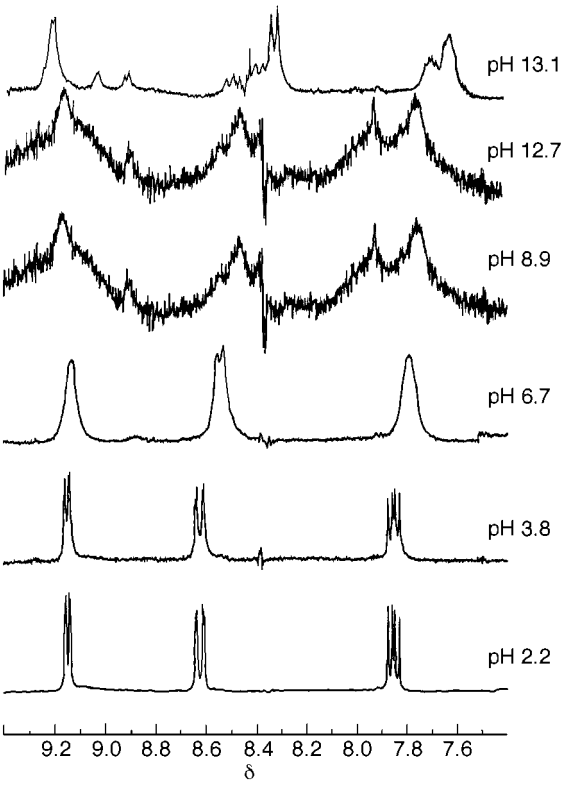


Fig. 3 Spectra showing the pH dependence of the signals of complex **2** in D_2O

Owing to the difficult electrochemical analysis of the new complexes it was not possible to draw conclusions about the effect of the different ligand substituents on the electrochemical properties of the ruthenium complexes. All six compounds and their proposed structures are summarized in Scheme 2.

Oxidation catalysis: general observations

Owing to the complicated electrochemical results it was not possible to study the catalytic oxidation capabilities of the complexes towards alcohols and sugars by cyclic voltammetry or by controlled-potential electrolysis as studied before by Gerli and Reedijk [5c] for the dinuclear ruthenium bpy complex. Therefore, the oxidation experiments were performed with chemical co-oxidants like $NaBrO_3$ for alcohols and O_2/aldehyde for the epoxidation of *trans*-stilbene. Most attention will be devoted to the reactions catalysed by the complex $[Ru_2(napy)_2(H_2O)_4Cl(OH)]^{4+}$ **2**, both because of its resemblance to the ruthenium–bpy dimer and for its more detailed structural characterization compared to those of the other new complexes.

Proton NMR spectra of catalyst **2** were taken at different pH. As can be seen in Fig. 3, the spectrum is best resolved at acidic pH. At more neutral pH the signals become broad and change to an apparent paramagnetic spectrum at pH 8.9. Only at extremely basic solution (pH 13.1), the signals become sharper again, albeit with the appearance of some additional species. When the pH of this solution is reversed from 13.1 to 2.2 the original spectrum, measured at pH 2.2, does not return, indicating that the conversion is irreversible. The transformation of the species obtained in acidic condition (pH 2.2) to species causing broader NMR signals at neutral conditions (pH 6.7) is fully reversible though. These experiments suggest that at acidic and neutral pH the complex is stable, which is contrary to the situation at basic pH.

A ^{31}P NMR spectrum of complex **2** in phosphate buffer displays two signals, at δ 4.23 and −11.25, respectively, shifted from the signal of non-co-ordinated phosphate, indicating two

types of co-ordination of phosphate to the ruthenium core.[27] A ^{1}H NMR spectrum of **2** in acetate buffer revealed one methyl signal at δ 2.61 that could be assigned to co-ordinated acetate, with an integral showing that two acetate groups are co-ordinated to one dinuclear complex. These results show that both acetate and phosphate can co-ordinate to complex **2**. However, these results suggest that two acetate molecules each replace two water molecules and bridge between the two ruthenium ions but that phosphate co-ordinates in two different modes to the ruthenium core, indicating at least other co-ordination modes than simple bridging.

Upon addition of a ten-fold excess of an alcohol to complex **2** in phosphate or acetate buffer no changes in the NMR spectrum were observed, showing the stability of **2** in the presence of an alcoholic group and no association between the alcohol and the complex, at least when the complex is present in the Ru^{III}_2 form. Upon addition of an excess of $NaBrO_3$ the three sharp signals of $H^{2,7}$, $H^{4,5}$ and $H^{3,6}$ disappear and six broad signals appear in the aromatic region at δ 9.04, 8.87, 8.51, 8.13, 7.48 and 7.21. After addition of an excess of an alcohol (for instance *n*-butanol) and stirring at room temperature for 1 d the three (somewhat broad) signals reappear at δ 9.44, 9.07 and 8.18, albeit shifted downfield compared to those of the original complex (δ 9.18, 8.62 and 7.83, respectively). This experiment suggests that the original symmetric complex is oxidized by $NaBrO_3$ to yield an asymmetric high-valent complex, which is subsequently reduced by an alcohol to yield again a symmetric complex.

Since the above-described experiments do not give quantitative information about the high-valent oxidation state of the catalyst, a spectrometric titration was done with Ce^{IV} as oxidant. The absorption spectrum of complex **2** in aqueous solution is characterized by a visible band at 393 nm which is characteristic of metal-to-ligand charge-transfer $d_\pi \longrightarrow \pi^*$ transitions. The MLCT band shifts to higher energy by 30 nm in 0.1 M CF_3SO_3H solution. A spectrophotometric titration of **2** with Ce^{IV} in 0.1 M CF_3SO_3H shows a two-electron oxidation of $[Ru^{III}Ru^{III}(napy)_2(H_2O)_4Cl(OH)]^{4+}$ to the Ru^{IV}_2 analogue, with an isosbestic point at 390 nm. A plot of the absorbance of **2** at 384 nm (also observed at other wavelengths) *vs.* the Ce:Ru mole ratio has an apparent end-point at Ce:Ru of 2 ± 0.2:1. Although the decrease is quite linear (correlation coefficient = 0.987), some of the deviation of linearity could be caused by disproportionation reactions of Ru^{IV}_2, similar to those of the dinuclear ruthenium–bpy complex. Addition of an excess of $NaBrO_3$ to the Ru^{III}_2 species gives a similar absorbance spectrum [as of the high-valent complex obtained with cerium, λ (ε × 10^2) = 254 (344), 300 (288) and 374 nm (109 M^{-1} cm^{-1})], however at a slower rate. Addition of an excess of alcohol to this solution causes the return of the original low-valent species [λ (ε × 10^{-2}) = 258 (243), 305 (109) and 393 nm (96 M^{-1} cm^{-1})].

To study the mechanistic features of this reaction in some more detail, cyclobutanol was treated in the catalytic system (co-oxidant $NaBrO_3$). Over a wide range of pH (3–11) both cyclobutanone and acyclic products were found as reaction products at all pH, which indicates that the catalytic system can operate *via* both a one- and two-electron transfer in the oxidation step.[28] The absorption results and the cyclobutanol oxidation result suggest that the Ru^{III}_2 complex is oxidized to Ru^{IV}_2 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}_2, thereby oxidizing alcoholic substrates.

Although catalytic characteristics of the other complexes have also been studied, a detailed discussion is less relevant because of limited information about their exact structures in water. In fact the poor solubility in water and organic solvents allowed only limited oxidation studies with $Ru_2(ppyz)_2(dmso)_2Cl_4$ and $Ru_2(napy)_2Cl_4$.

Table 2 Oxidation of cyclohexanol by $NaBrO_3$, catalysed by several ruthenium complexes at 60 °C for 15 h. Ratio catalyst:substrate:$NaBrO_3$ is 1:1000:4000; 100% selectivity for cyclohexanone

	Catalyst	Conversion (%) (turnovers)
2	$[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4\cdot 3H_2O$	41 (410)
3	$Ru_2(ppyz)_2(dmso)_2Cl_4(H_2O)_3$	73 (730)
4	$Ru_2(dmnapy)Cl_4$	70 (700)
5	$Ru_2(dcnapy)Cl_4$	89 (890)
6	$Ru(danapy)Cl_2(H_2O)_2$	55 (550)
7	$Ru_2(danapy)Cl_6(H_2O)_4$	80 (800)

Table 3 Oxidation of *n*-butanol by $NaBrO_3$, catalysed by several ruthenium complexes at room temperature for 15 min. Ratio catalyst:substrate:$NaBrO_3$ is 1:1000:2000

Catalyst	Conversion (%) (turnovers)	Products (%)
2	9 (90)	Butyraldehyde (1.5) Butyric acid (7.5)
3	35 (350)	Butyric acid (35)
4	94 (940)	Butyraldehyde (2.5) Butyric acid (91.5)
5	72 (720)	Butyraldehyde (12.5) Butyric acid (58.5)
6	90 (900)	Butyraldehyde (2) Butyric acid (57) Propanoic acid (31)
7	89 (890)	Butyraldehyde (1.5) Butyric acid (44) Propanoic acid (43.5)

Catalytic oxidation of alcohols

Complexes **2** through **7** were tested for their catalytic activity in the oxidation of a primary and a secondary alcohol (Table 2). Cyclohexanol was chosen as an aliphatic secondary alcohol and $NaBrO_3$ as the terminal oxidant. All catalysts showed a catalytic activity for this substrate, yielding only cyclohexanone. The mononuclear danapy complex appears to be less active than the dinuclear danapy catalyst.

As a primary alcohol, *n*-butanol was selected. All complexes show a high or very high activity towards *n*-butanol. The dmnapy complex **4** is especially active with 940 turnovers in 15 min at room temperature. Complexes **2** and **3** show a lower catalytic activity towards this substrate than do the other complexes (Table 3). A difference in selectivity between the danapy complexes on one side and the other complexes on the other is observed. The danapy complexes show, besides alcohol oxidation activity, also carbon–carbon bond cleavage, while the other catalysts only yield butyraldehyde and butyric acid. In contrast to what is found for cyclohexanol (see above) the mononuclear danapy complex is as active as the dinuclear danapy complex.

A detailed comparison of the results obtained in oxidations of these substrates with various primary oxidants in combination with ruthenium catalysts with literature data is difficult. A major problem is that reaction conditions (solvent, reaction time, reaction temperature, amount and type of co-oxidant) are not comparable. In Table 4 the number of turnovers per hour of the dcnapy complex towards cyclohexanol is compared to literature results.[29,30] From this comparison one can conclude that the dcnapy complex seems quite reactive in the sense that it shows more turnovers per hour than the other complexes. It should be realized, however, that this high activity is seen at a

Table 4 Oxidation of secondary alcohols, catalysed by different ruthenium complexes

Catalyst	*T*/°C	Ref.	Turnovers per hour	Co-oxidant	Solvent
$[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ [a]	r.t.	30(*a*)	8	NBu_4IO_4	CH_2Cl_2
$[RuO_2(HIO_6)_2]^{6-}$ [a]	r.t.	30(*b*)	19	NBu_4IO_4	CH_2Cl_2
$[PPh_4][RuO_2(O_2CMe)Cl_2]$ [b]	r.t.	30(*c*)	18	mmo [c]	CH_2Cl_2
$[Ru_2O_6(py)_4]\cdot 3.5H_2O$ [a]	r.t.	30(*d*)	20	mmo	MeCN
$[HNC_5H_4Bu^t\text{-}4][RuO_2Cl_3(NC_5H_4Bu^t\text{-}3)]$ [a]	r.t.	30(*d*)	6	mmo	MeCN
cis-$[Ru(dcbpy)_2(OH_2)_2]^{2+}$ [d]	r.t.	30(*e*)	20	*e*	Water
$[Ru_2(dcnapy)Cl_4]$ [a]	60 °C	*f*	59	$NaBrO_3$	Water

r.t. = Room temperature. [a] Cyclohexanol as substrate. [b] Cyclooctanol as substrate. [c] *N*-Methylmorpholine *N*-oxide. [d] dcbpy = 6,6′-Dichloro-2,2′-bipyridine; cyclobutanol as substrate. [e] Electrooxidation, glassy carbon electrode. [f] This study.

higher temperature and another co-oxidant than for the other complexes and in water instead of acetonitrile or methylene chloride.

Epoxidation of *trans*-stilbene

The catalytic epoxidation of olefins is both an important industrial technology and a useful synthetic method,[31] and several catalytic epoxidation systems are known using $RuCl_3$ with bipyridyl or substituted phenanthrolines.[32] The most effective catalyst to date is that reported by the group of Griffith,[30a] $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$, which is able to epoxidize *trans*-stilbene with 100% selectivity to *trans*-stilbene oxide with 249 turnovers in 15 h at 2 °C, with $NaIO_4$ as a co-oxidant. From an environmental and economical point of view dioxygen or hydrogen peroxide would be better co-oxidants to use. However, hydrogen peroxide is known to be easily decomposed on ruthenium and has therefore to be used in a large (100-fold) excess to yield reasonable amounts of product.[33] The use of molecular oxygen in the liquid-phase synthesis of organic compounds is limited because its triplet ground state precludes reaction with singlet organic compounds. Recently,[34] metal (including ruthenium)-catalysed epoxidations have been described with the use of a combination of an aldehyde and dioxygen. Mechanistically these systems are rather complex as several species present in the reaction mixture might effect the epoxidation of the olefin.[35] The mechanism of epoxidation is generally believed to proceed by the autoxidation of butyraldehyde to peracids and alkyl hydroperoxides, which can then be used as oxygen-transfer agents in the epoxidation of alkenes. Besides epoxidation a notorious side reaction is oxidative cleavage of the double bond, yielding two aldehyde molecules. Ruthenium dioxide without amine ligands present is known selectively to catalyse oxidative cleavage of carbon–carbon bonds of terminal and α/β unsaturated carbonyl compounds using molecular oxygen/aldehyde to give the corresponding carbonyl compounds.[36] It is known that the selectivity of the epoxidation reaction can be improved by the addition of amine ligands to the reaction mixture, or by the use of ruthenium amine complexes.[35d]

All novel catalysts are tested for their activity in the epoxidation reaction of *trans*-stilbene. With $NaBrO_3$ or $NaIO_4$ as co-oxidants only small amounts of epoxide are formed with benzaldehyde being a major side product. When dioxygen is used in a free-radical autoxidation better selectivities for the epoxide are obtained (see Table 5). All complexes proved to be active for high turnovers (from 90 for the ppyz complex to 950 for the dcnapy complex) in 20 h under mild conditions. It cannot be excluded that the complexes act as radical initiators for an autoxidation reaction (epoxidation *via* RCO_3). However the fact that the different complexes show not only different catalytic rates but also different selectivities (from 58 to 98%) suggests more involvement of the ruthenium complexes in the mechanism than being just a radical initiator.

As can be seen in Table 5, the dinuclear complexes appear to be less reactive than the mononuclear complexes. The ppyz complex is the poorest catalyst and the dcnapy complex (which is easily converted into a mononuclear complex in aqueous solution as discussed before) is the most reactive catalyst for epoxidation with the mononuclear danapy complex as second best. The dinuclear napy, danapy and dmnapy complexes (the latter is known to keep its structure in solution as discussed) all give a lower yield of epoxide.

Table 5 Epoxidation of *trans*-stilbene by O_2/butyraldehyde, catalysed by several ruthenium complexes at 40 °C for 20 h

Catalyst	Conversion (%) (turnovers)	Selectivity for epoxide (%)
2	42 (420)	81
3	9 (90)	98
4	18 (180)	73
5	95 (950)	87
6	91 (910)	78
7	38 (380)	58

In conclusion the mononuclear danapy and dcnapy complexes are quite active catalysts for the epoxidation reaction with a reactivity comparable to the data reported for $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$. Their selectivity for the epoxidation reaction compared to carbon–carbon cleavage is quite good, although lower than reported[30a] for $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$.

Conclusion

Although the complexes described in this paper were originally synthesized with the aim to obtain a series of dinuclear complexes only different in their electrochemical characteristics, several types of complexes were isolated. Seven new complexes which were characterized by NMR, Fourier-transform IR, UV/VIS spectroscopy and subjected to electrochemical study. According to their properties they have been divided into three subgroups.

Group I consists of ruthenium dinuclear complexes having two ligands co-ordinated to two ruthenium atoms, **3** and **1** and the aquated derivative **2**. Group II consists of ruthenium dinuclear complexes having only one ligand co-ordinated to two ruthenium atoms, **4** and **5**. Proton NMR spectra for both complexes in aqueous solution and in acetonitrile reveal the conversion of a symmetrical form, indicating a conversion into dinucleating behaviour of the ligand, into an asymmetrical form, suggesting mononucleating behaviour of the ligand. Group III consists of a mono- and a di-nuclear complex with the ligand danapy, **6** and **7** (see Scheme 2 for the suggested structural formulae of the new complexes according to the obtained analytical data). The electrochemical analysis did not allow conclusions about the effect of the different ligand sub-

stituents on the electrochemical properties of the ruthenium complexes.

The novel naphthyridine complexes have been tested for their catalytic reactivity in the oxidation of cyclohexanol, *n*-butanol and the epoxidation of *trans*-stilbene. All complexes prove to be quite reactive towards aliphatic primary and secondary alcohol oxidation. For the primary alcohol oxidation, the danapy complexes show an additional carbon–carbon bond cleavage reactivity compared to the other complexes. For catalyst **2** NMR and spectrophotometric data suggest that the symmetric Ru^{III}_2 core is oxidized by a two-electron step to an asymmetric Ru^{IV}_2 oxo complex, which in turn oxidizes the substrate, thereby being reduced again to a symmetric Ru^{III}_2 complex. From the results of the epoxidation reaction of *trans*-stilbene it can be concluded that dinuclear complexes (which retain their dinuclear structure in aqueous solution) are less active than the mononuclear complexes (or dinuclear complexes that become mononuclear in aqueous solution). The catalysts have a selectivity for the epoxide between 73 (complex **7**) and 99% (complex **3**), using environmental friendly dioxygen/butyraldehyde as co-oxidant/reductant.

Experimental

Reagents and substrates

The compound $RuCl_3(H_2O)_x$ (x is approximately 3) was used as obtained on a loan scheme from Johnson Matthey. 1,8-Naphthyridine was prepared as reported by Paudler and Kress.[37] Other chemicals were purchased (analytical grade) and used without further purification or were prepared as described below. For analytical measurements Millipore water was used.

Ligand synthesis

2,7-Dihydroxy-1,8-naphthyridine. A suspension was prepared of finely ground 2-amino-7-hydroxy-1,8-naphthyridine (20.0 g, 124 mmol) in concentrated sulfuric acid (200 cm^3) in a round-bottomed flask (500 cm^3) containing a stir bar. The flask was placed in an ice-bath and finely ground sodium nitrite (10.6 g, 124 mmol) added. The solution was stirred for 15 min and poured over crushed ice. It was made neutral by the addition of saturated sodium carbonate solution, causing the precipitation of a yellow-brown solid. The solid was filtered off, washed well with water and air dried. The yield of the product was 15.2 g (76%) and though contaminated by about 5% of the starting material was sufficiently pure to be used in the next step. ^{1}H NMR [$(CD_3)_2SO$ *vs.* $SiMe_4$]: δ 7.78 (d, J = 9, 2 H), 6.28 (d, J = 9 Hz, 2 H) and 3.21 (br s, 2 H).

2,7-Dichloro-1,8-naphthyridine (dcnapy). A flask was charged with finely ground dry 2,7-dihydroxy-1,8-naphthyridine (8.0 g, 50 mmol). The reaction vessel was cooled in ice and phosphorus pentachloride (24.4 g, 100 mmol) added, followed by phosphorus trichloride oxide (16.2 g, 1.5 mmol). After the initial exothermic reaction had subsided the cooling bath was removed and the reaction mixture refluxed for 3 h. The reaction was cooled and ice (≈300 g) was added. The product was filtered off, washed well with water and air dried to yield 2,7-dichloro-1,8-naphthyridine (7.3 g, 73.8%) as a solid. This material was found to be pure according to ^{1}H NMR spectroscopy [$(CD_3)_2SO$ *vs.* $SiMe_4$]: δ 8.15 (d, J = 9, 2 H) and 7.61 (d, J = 9 Hz, 2 H).

2,7-Dimethoxy-1,8-naphthyridine (dmnapy). A solution of sodium methoxide in methanol was prepared by dissolving sodium metal (2.32 g, 100 mmol) in dry methanol (300 cm^3). To this was added 2,7-dichloro-1,8-naphthyridine (5.0 g, 25 mmol). The suspension was heated at reflux under an atmosphere of argon for 4 h, cooled and filtered to remove sodium chloride. The methanol was removed under reduced pressure. The off-white solid was dissolved in the minimum volume of methylene chloride and passed through a plug of neutral alumina. The solvent was removed and the product recrystallized from the minimum volume of methanol, yield 3.6 g, 72.4%. ^{1}H NMR [$(CD_3)_2SO$ *vs.* $SiMe_4$]: δ 8.21 (d, J = 9, 2 H), 6.94 (d, J = 9 Hz, 2 H) and 4.01 (s, 3 H). M.p. 73 °C.

2,7-Di(phenylazo)-1,8-naphthyridine (danapy). A suspension was prepared of finely ground 2,7-diamino-1,8-naphthyridine (0.4 g, 2.5 mmol) in an aqueous sodium hydroxide–benzene mixture (10 g of NaOH in 30 cm^3 of water and 15 cm^3 of benzene). To this was added nitrosobenzene (1.6 g, 15.6 mmol) as a solid in one portion. The green suspension was heated to 50 °C for 90 min, cooled and diluted with water (80 cm^3). Extraction with methylene chloride (4 × 100 cm^3) yielded a brown solution, which was dried over $MgSO_4$ and the solvent removed. The dark solid was chromatographed on neutral alumina with methylene chloride. A bright green band eluted quickly from the column and was discarded. A second orange band was recovered, and the solvent removed to yield 2,7-di(phenylazo)-1,8-naphthyridine as an orange powder (260 mg, 22%). This material was sufficiently pure to be used without further purification. ^{1}H NMR ($CDCl_3$ *vs.* $SiMe_4$): δ 8.45 (d, J = 9, 2 H), 8.16 (m, 4 H), 8.09 (d, J = 9, 2 H), 7.60 (dd, J = 3, 4 Hz, 4 H) and 7.52 (m, 2 H).

Complex synthesis

$Ru_2(napy)_2Cl_4$. 1,8-Naphthyridine (225 mg), $RuCl_3(H_2O)_3$ (480 mg) and LiCl (700 mg) were dissolved in methanol (60 cm^3) and refluxed for 5 h. After cooling a precipitate was filtered off. After the solid was extracted five times with boiling water, it was dried under reduced pressure yielding a yellow compound **1**. Yield 937 mg (91%). ^{1}H NMR [$(CD_3)_2SO$ *vs.* $SiMe_4$]: δ 9.88 (br s, 2 H), 8.51 (br s, 2 H) and 7.80 (br s, 2 H).

$[Ru_2(napy)_2(H_2O)_4Cl(OH)][ClO_4]_4$. The compounds $Ru_2(napy)_2Cl_4$ (100 mg) and $AgClO_4$ (120 mg) were dissolved in water–acetone (1:3 v/v, 100 cm^3) and refluxed for 2 h. After cooling, the solution was filtered and reduced in volume to 10 cm^3, under reduced pressure. This solution was allowed to stand at room temperature for at least 1 week under air until green crystals of complex **2** precipitated. Yield 83 mg (51%). ^{1}H NMR [D_2O *vs.* dds (4,4-dimethyl-4-silapentane sulfonic acid)]: δ 8.92 (d, J = 5, 2 H), 8.56 (d, J = 9, 2 H) and 7.81 (t, J = 7 Hz, 2 H).

$Ru_2(ppyz)_2(dmso)_2Cl_4$. The compounds $RuCl_3(H_2O)_3$ (126 mg), pyrido[2,3-*b*]pyrazine (68 mg) and LiCl (200 mg) were dissolved in methanol (20 cm^3) and refluxed for 7 h. After cooling, the precipitate was filtered off and redissolved in the minimum volume of dmso (3 cm^3). This solution was allowed to stand at room temperature for some days until red crystals of complex **3** precipitated. Yield 40 mg (11%). ^{1}H NMR [$(CD_3)_2SO$ *vs.* $SiMe_4$]: δ 9.52 (m, 1 H), 9.46 (dd, J = 9, 1 H), 9.11 (dd, J = 9, 1 H), 8.56 (t, J = 10 Hz, 1 H) and 8.05 (m, 1 H).

$Ru_2(dmnapy)Cl_4$. The compounds dmnapy (62 mg) and $RuCl_3(H_2O)_3$ (85 mg) were dissolved in ethyl acetate (10 cm^3) and refluxed for 2 h. The brownish red precipitate of complex **4** was filtered off, washed with several portions of ethyl acetate and cold methanol and dried under reduced pressure. Yield 84 mg (49%). ^{1}H NMR (D_2O *vs.* dds): δ 8.50 (d, J = 9, 2 H), 7.25 (d, J = 9 Hz, 2 H) and 4.23 (s, 6 H).

$Ru_2(dcnapy)Cl_4$. This complex was synthesized by the same procedure as $Ru_2(dmnapy)Cl_4$ **5**. Yield 57%. ^{1}H NMR (D_2O *vs.* dds): δ 8.49 (d, J = 9, 2 H) and 7.76 (d, J = 9 Hz, 2 H).

Ru(danapy)Cl_2 and Ru_2(danapy)Cl_6. The compounds danapy (110 mg) and $RuCl_3(H_2O)_3$ (177 mg) were dissolved in methanol (20 cm^3) and refluxed for 2 h. After cooling a red crystalline precipitate was filtered off and dried under reduced pressure. To the filtrate, reduced in volume under reduced pressure to 5 cm^3, was added diethyl ether (200 cm^3). After standing overnight at 4 °C a green microcrystalline product precipitated, which was filtered off and dried under reduced pressure. Yield red precipitate, Ru(danapy)Cl_2 **6**, 61 mg (34%). ^{1}H NMR (CD_3OD *vs.* $SiMe_4$): δ 8.72 (d, J = 8, 1 H), 8.54 (d, J = 9, 1 H), 8.46 (d, J = 8, 1 H), 8.37 (d, J = 9, 1 H), 8.25 (m, 2 H), 8.08 (br d, J = 7, 2 H), 7.70 (m, 4 H) and 7.55 (t, J = 7 Hz, 2 H). Yield green precipitate, Ru_2(danapy)Cl_6 **7**, 22 mg (8.9%). ^{1}H NMR (CD_3OD): δ 8.37 (t, J = 10, 2 H), 8.23 (d, J = 9, 1 H), 8.09 (d, J = 9, 2 H), 7.94 (m, 1 H), 7.90 (m, 1 H), 7.66 (d, J = 8, 2 H), 7.56 (m, 3 H) and 7.44 (d, J = 9 Hz, 1 H).

Analytical methods

The apparatus for ^{1}H NMR, cyclic voltammetry and UV/VIS spectroscopy has been described before.[26] Elemental analyses were performed by the microanalytical laboratory of the University of Groningen. Ruthenium complexes are notorious for causing problems in complete combustion analyses. Also in this case we needed a slightly higher error window (maximum error of 0.8% *versus* a normal maximum error of 0.5%) to explain our data. Fourier-transform infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer spectrometer (Paragon 1000) in ultrapure caesium iodide (Johnson Matthey) or polyethylene. Spectrophotometric redox titrations were carried out by adding aliquots of a 1.8×10^{-3} M solution of Ce^{IV} in 0.1 M CF_3SO_3H to aliquots (0.5 cm^3) of a 3.1×10^{-4} M solution of complex **1** in 0.1 M CF_3SO_3H. The volume was adjusted to 3 cm^3 by addition of 0.1 M CF_3SO_3H, and the changes were monitored in the range 200–600 nm. The Ce : Ru mole ratio was varied from 0 to 6 : 1. Cerium(IV) solutions in 0.1 M CF_3SO_3H were prepared from $[NH_4]_2[Ce(NO_3)_6]$.

Catalytic procedure for the oxidation of alcohols

All catalytic reactions were conducted under dioxygen. Specific blank experiments did not show any activity towards the substrate unless stated otherwise. All reaction substrates were analysed by gas chromatography and found to be satisfactory compared to commercial samples. Specific procedures have been described for *n*-butanol and cyclohexanol oxidation.[26] A general example is as follows: substrate (100 mg) was dissolved in water (5 cm^3) after which 4 molar equivalents of $NaBrO_3$ and 0.001 molar equivalent of ruthenium complex were added. The reaction mixture was stirred at the desired temperature and for the desired time after which it was extracted with ether and methylene chloride (in order to extract the substrate and products which did not contain an acid group), acidified and again extracted (in order to extract the products which contain an acid group). The organic layers were dried over $MgSO_4$ and analysed by gas chromatography. To increase solubility of $Ru_2(ppyz)_2(dmso)_2Cl_4$, 10% v/v dmso was added to solutions in which this complex was used as a catalyst.

Catalytic procedure for the epoxidation of *trans*-stilbene

The conditions for the oxidation of *trans*-stilbene were as follows. In the case of $NaBrO_3$ or $NaIO_4$ as a co-oxidant, *trans*-stilbene (0.15 mmol), catalyst (0.15×10^{-3} mmol) and $NaBrO_3$ or $NaIO_4$ (0.3 mmol) were dissolved in a mixture of water (2 cm^3) and 1,2-dichloroethane (2 cm^3). This mixture was stirred for 24 h at 40 °C. In the case of dioxygen as a co-oxidant, *trans*-stilbene (0.15 mmol), isobutyraldehyde (54 μl) and catalyst (0.15×10^{-3} mmol) were dissolved in a vigorously stirred mixture of water (2 cm^3) and 1,2-dichloroethane (2 cm^3). This mixture was stirred for 24 h at 40 °C. Blank experiments without the ruthenium catalyst yielded at most 10% conversion under the same reaction conditions.

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