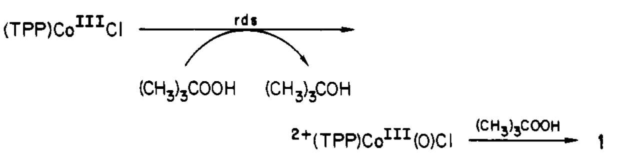
ligand and nucleophilic substitution by *tert*-butyl hydroperoxide on this dication, analogous to CH_3OH attack on the electrochemically generated $^{2+}(TPP)Co^{III}Cl$, would be possible (eq 6).


(6)

The break in the linear free energy relationship shown in Figure 3 suggests to us a mechanistic difference between the percarboxylic acids and the alkyl hydroperoxides. On this basis we prefer the rate-determining homolytic cleavage mechanism of eq 5 for the reaction of *tert*-butyl hydroperoxide with $(TPP)Co^{III}Cl$.

With $(TPP)Cr^{III}Cl$, $(TPP)Mn^{III}Cl$, and $(TPP)Fe^{III}Cl$, oxygen atom transfer from percarboxylic acids and alkyl hydroperoxides results in intermediates in which the metal is raised to the oxidation state of M^V or M^{IV}. These intermediates are sufficiently stable toward nucleophiles in the presence of an appropriate substrate to function as oxygen-transfer catalysts. This is not the case with $(TPP)Co^{III}Cl$. The ready formation of isoporphyrin complexes from the cobalt intermediate in the presence of trace concentrations of nucleophiles is compatable with the localization of the oxidizing equivalents on the porphyrin ligand rather than on the metal. The cobalt is a very active participant in the oxygen-transfer reaction, as evidenced by the exceedingly large second-order rate constants for oxygen transfer from the percarboxylic acids. Although Co(III) is oxidized to Co(IV) with great reluctance, being limited primarily to fluoro and oxo complexes,[7] the rate constants for reaction of the percarboxylic acids and $(TPP)Co^{III}Cl$ are 2 orders of magnitude greater than those obtained with $(TPP)Cr^{III}Cl$ and $(TPP)Fe^{III}Cl$, a further indication that the porphyrin ligand is supplying the electrons. Electrochemical studies of organobis(dimethylglyoximato)cobalt(III) complexes demonstrate that the principal site of one-electron removal is the cobalt atom.[26] In this same study, based on kinetic measurements for the chemical oxidation of these complexes, the authors conclude that the electron may initially be removed from the ligand followed by structural rearrangement and internal electron transfer to yield the Co(IV) species. With an electron-rich porphyrin ligand, an opposite effect can be imagined wherein initial transfer of an oxygen atom to cobalt(III) yields a higher valent cobalt(V) species which by rapid internal electron transfer results in the porphyrin dication species (eq 7). On the other hand, the intermediate structures depicted

$$(TPP)Co^{III}\text{-}Cl + RCO_3H \rightarrow [(TPP)Co^V(O)Cl] \rightarrow {}^{2+}(TPP)Co^{III}(O)Cl \quad (7)$$

$$(TPP)Co^V(O)Cl \leftrightarrow {}^{\cdot+}(TPP)Co^{IV}(O)Cl \leftrightarrow {}^{2+}(TPP)Co^{III}(O)Cl \quad (8)$$

in eq 7 could also be simply limiting forms of the same structure (eq 8). The extremely high reactivity of the intermediate toward nucleophiles suggests that the porphyrin dication is the predominant intermediate structure.

Several cobalt(III) complexes with an alkyl hydroperoxide bonded directly to the cobalt have been characterized. A recent report on the thermal decomposition of the *t*-BuOO–cobalt(III) 1,3-bis(pyridylimino)isoindoline complex demonstrated a homolytic decomposition of the O–O bond of the peroxide.[27] In contrast to the electron-rich porphyrin ligand the 1,3-bis(pyridylimino)isoindole ligand was not oxidized and the oxidation equivalent resided in the cobalt–oxo moiety (species reacts as if it were Co^{III}–O·).

The likely formation of a cobalt porphyrin dication species upon oxygen atom transfer to $(TPP)Co^{III}Cl$ completes an interesting series. Oxygen atom transfer to $(TPP)Cr^{III}Cl$, $(TPP)Mn^{III}Cl$, $(TPP)Fe^{III}Cl$, and $(TPP)Co^{III}Cl$ results in intermediate metal–oxo species that go from primarily metal-centered to what our data suggest is mainly a metal–oxo porphyrin-centered oxidation. With chromium and manganese, the pentavalent metal–oxo species are formed. In the case of iron, one oxidizing equivalent is localized on the metal and the other on the porphyrin, resulting in an iron(IV)–oxo porphyrin π cation radical, and with cobalt, the cobalt(III) porphyrin dication appears to be the primary product.

Acknowledgment. This stuudy was supported by a grant from the National Institutes of Health. We wish to thank Dr. Ata Shirazi for deteriming the 300-MHz ^1H NMR spectrum of compound **1**.

Registry No. 1, 99604-59-8; $(TPP)Cr^{III}Cl$, 60166-10-1; *t*-BuOOH, 75-91-2; CH_3OH, 67-56-1; O_2, 7782-44-7; *m*-chlorobenzoic acid, 937-14-4; *p*-nitroperbenzoic acid, 943-39-5; cumene hydroperoxide, 80-15-9; phenylperacetic acid, 19910-09-9; perlauric acid, 2388-12-7; diphenylhydroperoxyacetonitrile, 5233-67-0; diphenylhydroperoxyacetic acid, 60538-68-3; trityl hydroperoxide, 4198-93-0.

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Synthesis and Study of Mononuclear Ruthenium(II) Complexes of Sterically Hindering Diimine Chelates. Implications for the Catalytic Oxidation of Water to Molecular Oxygen

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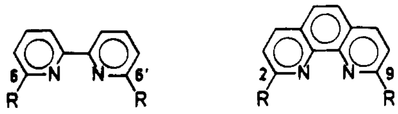
Bis(diimine) complexes of ruthenium(II) have been prepared. The chelates used are 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmp). Due to the steric hindrance created by the methyl groups α to the nitrogen atoms, the bis chelate complexes synthesized are all cis, with respect to the two remaining coordination sites, and cannot be photoisomerized to their trans isomers, in contrast with the equivalent complexes containing unsubstituted diimines. In addition, condensation of the mononuclear species to hydroxo- or oxo-bridged species of higher nuclearity is strictly prevented. The complexes have been characterized and studied by spectroscopic methods (UV–visible, IR, and ^1H and ^{13}C NMR). Their electrochemical behavior has been investigated in relation to the oxidation of water to molecular oxygen. The most significant results are the following: dinuclear species like $(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2{}^{4+}$ are required for catalytic generation of O_2 from water, in agreement with previously reported data.[7] On the other hand, the complexes presently reported display no activity toward oxidation of water.

Introduction

Oxidation of water to molecular oxygen is of great importance as a means for converting light energy into chemical energy. The practical value of the artificial systems presently available as models of water photosplitting is highly dependent on the ability of future systems to efficiently use H_2O as an electron donor.[1,2]

In addition, one of the most intriguing reactions taking place in natural photosynthesis is O_2 evolution by plants, the molecular mechanism of which is still obscure.[3] Various metallic oxides have been used in heterogeneous catalysis of water oxidation; in particular, extensive electrochemical studies of anodic materials have been performed.[4-6] Molecular systems capable of bringing about the oxidation of water to O_2 are extremely limited. It has been shown that aquo and oxo complexes of ruthenium could be used as catalysts for water oxidation.[7-9] The mononuclear compound *cis*-$Ru(bpy)_2(H_2O)_2^{2+}$ (bpy = 2,2′-bipyridine) was postulated as a homogeneous catalyst in O_2 formation,[10] but this complex undergoes a photoisomerization reaction,[11] leading to the inactive isomer *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$.[10] In order to both avoid isomerization problems, and to have at our disposition new mononuclear complexes able to catalyze water oxidation to O_2, we undertook the synthesis and study of compounds of the type $RuL_2(H_2O)_2^{2+}$, L being a geometrically constraining ligand such as 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmp). For those two ligands, the presence of sterically hindering methyl groups α to the nitrogen atoms prevents the formation of trans complexes and should therefore inhibit photoisomerization of cis compounds.



R = H: bpy
R = CH_3: 6,6′-dmbp

R = H: phen
R = CH_3: 2,9-dmp

Experimental Section

Materials. All solvents were of reagent grade and were used as received. For photochemical preparations and electrochemical experiments, high-purity methylene chloride and acetonitrile were obtained from Merck and were used without further purification. 6,6′-dmbp was synthesized as reported previously.[40] 2,9-dmp, bpy, and $RuCl_3 \cdot 3H_2O$ were obtained from EGA.

Measurements. ^1H and ^{13}C NMR spectra were all acquired on a Bruker WP 200 SY instrument and shifts are reported vs. Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 597 IR spectrophotometer for Nujol mulls between cesium iodide plates; visible and UV spectra were obtained on a Cary 219 spectrophotometer. Cyclic voltammetry and controlled-potential coulometry were carried out on a Bruker EI 310M potentiostat connected to a XY Ifelec IF 3802 recorder and a Tacussel IGSN integrator. All experiments were done under argon atmosphere in a three-electrode configuration by using a Tacussel platinum planar electrode, a glassy-carbon disk electrode, or a Metrohm hanging mercury electrode as the working electrode. The results were taken at room temperature (22 ± 2 °C) and are referenced to a saturated calomel electrode (SCE).

Measurements of dissolved O_2 in H_2O oxidation experiments were obtained by using an Orion oxygen electrode, Type 97.08. Dioxygen in the gas phase was analyzed by gas-phase chromatography with a Varian Aerograph 700 instrument fitted with a molecular sieve column at 25 °C. The carrier gas was high-purity methane. Elemental analyses were performed by the Service Central de Microanalyse du CNRS.

Synthesis of Complexes. *Caution*! Perchlorate salts of organometallic or organic cations might explode. Therefore, preparation and handling of some of the following compounds deserve particular care.

Preparation of $Ru(6,6'\text{-dmbp})(CO)Cl_2(DMF)\cdot{}^1/_2H_2O$, $[Ru(6,6'\text{-dmbp})_2(CO)(Cl)](ClO_4)$, and $[Ru(6,6'\text{-dmbp})_2(CH_3CN)_2](ClO_4)_2$. $RuCl_3 \cdot 3H_2O$ (1 g, 3.8 mmol), 6,6′-dmbp (1.5 g, 8.2 mmol), and LiCl (0.6 g, 14 mmol) were mixed in 10 mL of DMF, under argon. After the mixture was heated under reflux for 5 h and cooled down to room temperature and 10 mL of acetone added, the intense red solution was kept at 0 °C overnight. The yellow-orange microcrystalline solid obtained was filtered, washed with 5 mL of H_2O–acetone (3/2) and dried under vacuum (0.1 mmHg). Yield: 11% (0.2 g). The filtered solution was evaporated to dryness, and hot water (200 mL; 80 °C) was added to the residue. After filtration and cooling (ice bath), 10 mL of a concentrated $NaClO_4$ solution was added dropwise. The red-brown precipitate formed was filtered and roughly dried by an air flow through the frit; yield 1.5 g of solid. The latter was dissolved in 50 mL of CH_3CN and heated at 60 °C for 0.5 h. After the solvent was pumped off, the crude product obtained was subjected to chromatographic separation on neutral alumina (50 g), the eluent being a 50/50 mixture of toluene and CH_3CN. The composition of the fractions was monitored by thin layer chromatography (Al_2O_3; 1/1 toluene–CH_3CN as eluent). The first fractions contain some free ligand, the following orange fractions were collected and evaporated to dryness. The orange solid obtained was recrystallized in a CH_3CN–benzene (1/1) mixture. After filtration and drying under vacuum, 0.4 g (16%) of yellow crystals of $[Ru(6,6'\text{-dmbp})_2(CO)(Cl)][ClO_4]$ were obtained.

The last chromatographic fractions led to isolation of 0.48 g (16%) of $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2(ClO_4)_2 \cdot H_2O$ as yellow-orange crystals, after recrystallization in CH_3CN–benzene (1/1) and vacuum drying.

Preparation of $Ru(6,6'\text{-dmbp})_2Cl_2 \cdot 1.5CH_2Cl_2$. (a) Photochemical Method. In order to avoid any photoinduced redox reaction involving ClO_4^-, the latter anion was exchanged for PF_6^- as follows. $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2(ClO_4)_2$ (90 mg; 0.12 mmol) was dissolved in 4 mL of CH_3CN. An aqueous solution of NH_4PF_6 (1 g in 4 mL) was then slowly added. After addition of 20 mL of H_2O, the yellow precipitate was collected by filtration and redissolved in CH_3CN (10 mL). The solvent was evaporated under vacuum, and the solid obtained was dried (0.1 mmHg; room temperature; 15 min).

After dissolution of the yellow product in CH_2Cl_2 (50 mL) and addition of 0.15 g of $N(C_2H_5)_4^+Cl^-$, the photochemical reaction was performed. The solution was irradiated in a Pyrex Schlenk tube, under argon, for 4 h (halogen lamp, 150 W). The deep purple solution was concentrated to ~25 mL by evaporation, and diethyl ether (100 mL) was added. The purple precipitate that formed was collected by filtration and vacuum-dried. Yield: 90% (60 mg).

(b) Direct Method. $RuCl_3 \cdot 3H_2O$ (1 g, 3.8 mmol), 6,6′-dmbp (1.5 g, 8 mmol), and LiCl (2.2 g, 52 mmol) were added to 15 mL of ethylene glycol. The mixture was heated at 140 °C for 3 h, under argon. After the mixture was cooled down to room temperature, H_2O (10 mL) was added. The microcrystalline product obtained was collected by filtration, washed twice with 10 mL of chilled water, and vacuum-dried overnight. Yield: 87% (2.0 g).

UV-visible and ^1H NMR spectra were superimposable for samples prepared by the two different methods. The products analyzed correctly for $Ru(6,6'\text{-dmbp})Cl_2 \cdot 1.5CH_2Cl_2$.

Preparation of $Ru(6,6'\text{-dmbp})_2(H_2O)_2(ClO_4)_2 \cdot H_2O$. A 0.3-g sample of $Ru(6,6'\text{-dmbp})_2Cl_2 \cdot 1.5CH_2Cl_2$ (0.45 mmol) was dissolved in 10 mL of degassed water and heated at 60 °C under argon for 5 min. A saturated solution of $NaClO_4$ in 0.1 N $HClO_4$ (2 mL) was added dropwise. After the mixture was allowed to stand at 0 °C for 2 h, the precipitate was filtered off and dried under vacuum. Yield: 50% (170 mg). This preparation must be carried out in a relatively dark room. $Ru(6,6'\text{-dmbp})_2(H_2O)_2(PF_6)_2$ was prepared in a similar way, by addition of NH_4PF_6 to an aqueous solution of $Ru(6,6'\text{-dmbp})_2Cl_2 \cdot 1.5CH_2Cl_2$.

Preparation of $Ru(6,6'\text{-dmbp})_2(CN)_2 \cdot 3H_2O$. A 0.40-g sample of $Ru(6,6'\text{-dmbp})_2Cl_2 \cdot 1.5CH_2Cl_2$ (0.60 mmol) was dissolved in absolute ethanol (100 mL) containing 0.7 g of KCN (10 mmol). The solution was stirred at room temperature for 12 h, after which it was allowed to stand at 0 °C overnight. The intense red crystals obtained were collected by filtration, washed three times with 100 mL of H_2O, and dried under vacuum (0.2 mmHg) overnight. Yield: 66% (237 mg).

Preparation of $Ru(2,9\text{-dmp})_2Cl_2 \cdot H_2O$. A mixture of $RuCl_3 \cdot 3H_2O$ (1 g, 3.8 mmol), 2,9-dmp (1.7 g, 8 mmol), LiCl (2.5 g, 59 mmol), and ethylene glycol (15 mL) was heated at 150 °C for 6 h under argon. After the mixture was cooled down to room temperature and of water (5 mL) was added, a black-purple precipitate was obtained. It was collected by

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Table I. Elemental Analysis Data for 6,6′-dmbp and 2,9-dmp Ruthenium(II) Complexes

complex	% calcd			% found		
	C	H	N	C	H	N
Ru(6,6′-dmbp)(CO)Cl_2(DMF)·$^1/_2H_2O$	41.20	4.29	9.01	41.33	4.27	9.00
[Ru(6,6′-dmbp)$_2$(CO)Cl](ClO_4)	47.46	3.79	8.86	47.20	3.83	9.08
[Ru(6,6′-dmbp)$_2$(CH_3CN)$_2$](ClO_4)$_2$·H_2O	43.75	4.16	10.93	44.46	4.21	10.95
Ru(6,6′-dmbp)$_2Cl_2$·]1.5CH_2Cl_2	45.84	4.04	8.38	46.20	4.04	8.11
Ru(6,6′-dmbp)$_2$(H_2O)$_2$(ClO_4)$_2$·H_2O	39.88	4.15	7.75	39.87	4.01	7.56
Ru(6,6′-dmbp)$_2$(CN)$_2$·3H_2O	54.27	5.21	14.60	54.24	5.40	14.35
[Ru(2,9-dmp)$_2$(CH_3CN)$_2$](ClO_4)$_2$·2H_2O	46.06	4.07	10.07	46.07	4.15	9.90
Ru(2,9-dmp)$_2Cl_2$·H_2O	55.40	4.28	9.23	55.49	4.23	9.07

Table II. Electronic Properties of the Ruthenium(II) Complexes (L = 6,6′-dmbp, L′ = 2,9-dmp)

complex	UV and visible bands λ_{max}, nm ($10^{-3}\epsilon$, mol^{-1} L cm^{-1})					solvent
RuL(CO)(Cl_2)(DMF)		415 (1.68)	330 (17.6)	315 (17.0)	270 (25.0)	CH_3CN
RuL_2(CO)(Cl)$^+$		445 (1.80)	375	315 (23.0)	275 (22.0)	CH_3CN
$RuL_2(CN)_2$	482 (4.9)	418 (3.27)	302 (38.94)			MeOH
RuL_2Cl_2	560 (6.26)	380 (7.59)	312 (38.86)			CH_2Cl_2
$RuL_2(CH_3CN)_2^{2+}$	447 (6.60)	390 (3.9)	290 (52.8)			CH_3CN
$RuL_2(H_2O)_2^{2+}$	500 (8.06)		306 (46.7)		248 (17.25)	H_2O
cis-Ru(bpy)$_2(H_2O)_2^{2+}$	480 (13.4)	350 (9.8)	300			H_2O[11]
RuL'_2Cl_2	584 (6.89)	492 (5.42)		278 (45.0)	230 (57.5)	CH_2Cl_2
$RuL'_2(CH_3CN)_2^{2+}$	440 (6.87)	372 (6.52)		264 (53.47)	224 (48.7)	CH_3CN
$RuL'_2(H_2O)_2^{2+}$	496 (6.87)	412 (4.95)		270 (48.5)	224 (46.5)	H_2O
cis-Ru(phen)$_2(H_2O)_2^{2+}$	469 (10.7)			264 (83)	223 (55)	H_2O[11]

filtration and washed with H_2O (5 mL). After vacuum drying, 1.7 g (2.88 mmol) of a purple solid was obtained. Yield: 75%.

Preparation of Ru(2,9-dmp)$_2$(CH_3CN)$_2$(ClO_4)$_2$·2H_2O. A solution of Ru(2,9-dmp)$_2Cl_2$ (0.30 g) in CH_3CN (50 mL) was refluxed overnight under argon. A $NaClO_4$ solution in water (1 g in 5 mL) was slowly added to the cooled mixture. The orange precipitate obtained was collected by filtration. The crude solid contained a mixture of complexes, and it was subjected to a chromatographic separation. (alumina; 1/1 CH_3CN–toluene as eluent). A yellow product was isolated and recrystallized in a CH_3CN–benzene (1/1) mixture. After vacuum drying, 0.146 g of pure complex was obtained. Yield: 34%.

Preparation of [Ru(2,9-dmp)$_2$(H_2O)$_2$](ClO_4)$_2$. This compound was made in a manner similar to that used for its 6,6′-dmbp analogue.

Caution! While being dried at room temperature, under vacuum, an analytical sample (~15 mg) exploded extremely violently. Afterward, this compound was generated in situ and was no longer isolated as a solid.

Results and Discussion

(1) Preparation of the Complexes. The new complexes prepared are listed in Table I with their elemental analyses. The diaquo complexes of the type $RuL_2(H_2O)_2^{2+}$ are readily prepared by hydrolysis of the corresponding dichloro compounds, either by heating in slightly acidic medium[10] or by removal of the Cl's in the presence of Ag^+.[12] In order to synthesize the precursors Ru(6,6′-dmbp)$_2Cl_2$ and Ru (2,9-dmp)$_2Cl_2$, two procedures were used. The first method has been described earlier by Whitten et al.[13] and by Meyer et al.[14] Stoichiometric amounts of $RuCl_3$·3H_2O and of the ligand L are reacted in DMF (DMF = dimethylformamide) for 8 h under argon. With L = 6,6′-dmbp, this procedure allows isolation of the carbonylated compound Ru(6,6′-dmbp)(CO)Cl_2(DMF) in 11% yield, after crystallization of the crude solid obtained at the end of the reaction. Workup of the remaining mixture and chromatographic separation (alumina) lead to isolation of an additional carbonylated compound, [Ru(6,6′-dmbp)$_2$(CO)Cl](ClO_4) (yield 16%), as well as a bis(acetonitrile) complex, [Ru(6,6′-dmbp)$_2$(CH_3CN)$_2$](ClO_4)$_2$ (yield 16%). The formation of carbonylated complexes is not really surprising: Ru(bpy)$_2$(CO)Cl^+ has been obtained by treating $RuCl_3$·3H_2O with bpy in DMF under conditions similar to ours.[15,16] The only noticeable difference is the much longer reaction time required for the bpy complex prepared earlier.[16] The more hindering 6,6′-dmbp ligand greatly favors DMF decarbonylation. As already described in the literature for the bpy complex,[17] Ru(6,6′-dmbp)$_2$(CH_3CN)$_2^{2+}$ could be photochemically converted to Ru(6,6′-dmbp)$_2Cl_2$. The bis(acetonitrile) compound is thermally substitution-inert, even under quite severe conditions (reflux in water for several hours). Under light irradiation ($\lambda > 320$ nm) in a noncoordinating solvent, the two CH_3CN's are easily replaced by two Cl's, with a 90% yield. However, as the overall yield of Ru(6,6′-dmbp)$_2Cl_2$ was very poor (14%), we developed other synthetic routes. Methods based on reduced forms of ruthenium chloride or on "ruthenium blue"[18] and used previously by others to prepare tris chelated ruthenium(II) complexes of sterically hindered diimine ligands[19,20] turned out to be unsuccessful. On the other hand, by analogy to a procedure used by Dwyer et al.[21] for preparing osmium complexes of pyridine, the use of ethylene glycol as the reaction solvent led to excellent yields of the desired complexes. Ru(6,6′-dmbp)$_2Cl_2$ was obtained in 87% yield by heating a mixture of $RuCl_3$·3H_2O, LiCl, and 6,6′-dmbp at 140 °C in ethylene glycol for a few hours; similarly, Ru (2,9-dmp)$_2Cl_2$ was synthesized in 75% yield. The diaquo complexes Ru(6,6′-dmbp)$_2$(H_2O)$_2^{2+}$ and Ru(2,9-dmp)$_2$(H_2O)$_2^{2+}$ were obtained by simple dissolution of the corresponding dichloro complexes in aqueous medium (pH ~2). Solid salts were precipitated in the presence of a high concentration of the desired anion (ClO_4^-, PF_6^-, or BF_4^-). In the preparation of the diaquo compounds, two major difficulties have been encountered.

(i) In dilute nitric acid or perchloric acid, slow oxidation to ruthenium(III) takes place.[22] This process is highly light-accelerated, as for other ruthenium(II) complexes.[11] $RuL_2(H_2O)_2^{2+}$ solutions should thus preferably be handled in the dark and stored at low temperature.

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Table III. Infrared Spectral Data of the Ruthenium(II) Complexes (L = 6,6′-dmbp, L′ = 2,9-dmp)

complex	characteristic IR bands,[a] cm^{-1}
$RuL(CO)Cl_2(DMF)$	1940 (ν_{CO}), 1650 (L), 1250 (L), 1110, 800, 750, 700, 390, 320 (ν_{Ru-Cl})
$RuL_2(CO)Cl^+$	1950 and 1975 (ν_{CO}), 1570, 1610, 1250, 1090 ($\nu_{ClO_4^-}$), 800, 740, 620, 300 and 320 (ν_{Ru-Cl})
$RuL_2(CH_3CN)_2^{2+}$	1600, 1575, 1250, 1090 ($\nu_{ClO_4^-}$), 780, 730, 620
RuL_2Cl_2	1600, 1560, 1240, 1170, 1120, 1090, 1000, 810, 780, 730, 700, 520; 300, 280 (ν_{Ru-Cl})
$RuL_2(CN)_2$	2040 (ν_{CN}), 1590, 1560, 1230, 1170, 1110, 1090, 1030, 780, 730, 720
$RuL_2(H_2O)_2^{2+}$	1600, 1560, 1250, 1100 ($\nu_{ClO_4^-}$), 780, 720, 620
$RuL'_2(CH_3CN)_2^{2+}$	1620, 1580, 1500, 1340, 1310, 1215, 1150, 1080 ($\nu_{ClO_4^-}$), 850, 800, 720, 620, 550
RuL'_2Cl_2	1640, 1580, 1500, 1340, 1300, 1210, 1190, 1150, 850, 860, 840, 740, 550; 310 (ν_{Ru-Cl})
$RuL'_2(H_2O)_2^{2+}$	1630, 1580, 1500, 1280, 1220, 1050, 860, 730, 560, 530, 500

[a] Nujol mull, CsI plates.

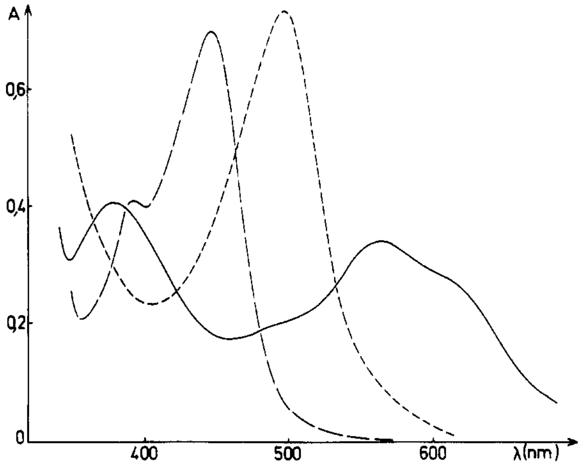

Figure 1. Electronic spectra of $Ru(6,6'\text{-dmbp})_2Cl_2$ (full line) in CH_2Cl_2, $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ (dotted line) in H_2O, and $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2^{2+}$ (dashed line) in CH_3CN.

(ii) *Caution*! An analytical sample of $Ru(2,9\text{-dmp})_2(H_2O)_2(ClO_4)_2$ exploded extremely violently while being dried under vacuum at room temperature.

Due to the lability of the two water molecules, the diaquo compounds are convenient precursors to other complexes: we could synthesize $Ru(2,9\text{-dmp})_2(CH_3CN)_2(ClO_4)_2$ and $Ru(6,6'\text{-dmbp})_2(CN)_2$, the latter being a weak photoemitter at room temperature in CH_3OH (λ_{em} = 620 nm; excitation at 482 nm); such a behavior is reminiscent of that of $Ru(bpy)_2(CN)_2$.[23,24]

(2) Spectroscopic Properties. (a) Electronic Spectra. UV and visible absorption data are collected in Table II. It is now well established that the intense low-energy absorption bands observed in $Ru(bpy)_2X_2$ (X = halide, CN^-, etc.[25,26]) are assigned to metal-to-ligand charge-transfer (MLCT) transitions of the type $d\pi(Ru) \rightarrow \pi^*(bipy)$. By analogy, the high extinction coefficients measured for the visible bands of the 6,6′-dmbp and 2,9-dmp complexes in Table II strongly support the MLCT nature of the corresponding transitions. The $\pi \rightarrow \pi^*$ transitions characteristic of the diimine ligands occur in the UV region of the various spectra. For each complex, the energy of the MLCT transition is highly dependent on the nature of ancillary ligands coordinated at the cis position. A large bathochromic shift is observed by replacing strong π-acceptors (CO, CN^-, CH_3CN) by less accepting ligands (H_2O, Cl^-). The redox potentials of the Ru^{III}/Ru^{II} couples (see Table V) are directly related to the strength of the π-back-donation: highly positive values are obtained for complexes containing acidic ligands. Some typical electronic spectra are shown in Figure 1. Generally, replacing bpy or phen ligands by 6,6′-dmbp or 2,9-dmp respectively induces a red shift (20–30 nm) of the MLCT band.

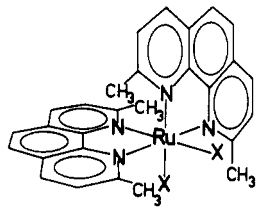

Figure 2. Proposed structure of $Ru^{II}(2,9\text{-dmp})_2X_2^{2+}$ in solution.

(b) IR Spectra. The most characteristic IR data of the complexes synthesized are indicated in Table III. They confirm the presence of the various ligands coordinated to the ruthenium atom as well as their binding mode. In particular, for the chloride-containing complexes $Ru(6,6'\text{-dmbp})(CO)Cl_2(DMF)\cdot{}^1/_2H_2O$, $Ru(6,6'\text{-dmbp})_2(CO)Cl(ClO_4)$, $Ru(6,6'\text{-dmbp})_2Cl_2$, and $Ru(2,9\text{-dmp})_2Cl_2$, ν_{Ru-Cl} frequencies are found between 280 and 320 cm^{-1}, clearly showing that the Cl's are indeed coordinated to the ruthenium atom. Comparable values have been observed for $Ru(Me_2SO)_4Cl_2$[27] (Me_2SO=dimethyl sulfoxide) and $Ru(bpy)_2Cl_2$.[28] The two carbonylated complexes contain terminal CO's, as indicated by the ν_{CO} frequency values (1940–1975 cm^{-1}). For comparison, ν_{CO} = 1965 cm^{-1} for the previously studied terminal carbonyl complex $Ru(bpy)_2(CO)Cl^+$.[29] In the spectrum of $Ru(6,6'\text{-dmbp})_2(CN)_2\cdot 3H_2O$, a sharp and intense band at 2040 cm^{-1} (shoulder at 2060 cm^{-1}) is observed: it is assigned to bound CN^-. The ν_{CN} value is almost identical with that earlier found for $Ru(bpy)_2(CN)_2$.[30] In contrast to the pentaammine complexes of ruthenium(II), bearing a benzonitrile or an acetonitrile ligand,[31] the bis(acetonitrile) complexes $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2^{2+}$ and $Ru(2,9\text{-dmp})_2(CH_3CN)_2^{2+}$ show broad bands of low intensity in the 2100–2300-cm^{-1} region. These bands are likely to correspond to bound CH_3CN.

For all the complexes studied, one observes the IR bands characteristic of the diimine ligand, the frequencies being slightly shifted with respect to those of the free ligand (see Table III).

(c) ^1H and ^{13}C NMR Data. NMR data are shown in Table IV. ^1H and ^{13}C NMR spectra provided clear evidence that all the bis(diimine) complexes studied are cis isomers, as represented in Figure 2. The geometry, as found by NMR spectroscopy, is not surprising due to the presence of CH_3 substituents α to the nitrogen atoms of the chelates used. The two X ligands being located at cis positions, the molecular symmetry of the complex in solution is C_2. In such an arrangement, the two pyridinic subunits of each 6,6′-dmbp chelate are not identical; on the other hand, each pyridine nucleus of a given 6,6′-dmbp is transformed into its homologue in the other 6,6′-dmbp by rotation about the C_2 axis.

NMR data are in agreement with the symmetry properties. For instance, in the case of $Ru(2,9\text{-dmp})_2(H_2O)_2^{2+}$, the methyl groups give rise to two signals (1.53 and 2.53 ppm) and the 7–8.5 ppm region shows 3 different AB systems (3,4; 5,6; 7,8) characteristic of a disymmetric substituted phenanthroline. Similarly, whereas the free ligand 6,6′-dmbp shows one triplet and two doublets for the H_4, H_3, and H_5 protons, respectively, the ^1H NMR spectrum of $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ is more complicated and contains two triplets and four doublets, demonstrating the loss of symmetry

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Table IV. ^1H and ^{13}C NMR Spectral Data of 6,6′-dmbp (L), 2,9-dmp (L′), and Their Ruthenium(II) Complexes

species	^1H NMR,[a] δ_{CH_3}	solvent	^{13}C NMR,[a] δ_{CH_3}	solvent
L	2.58	$CDCl_3$	24.71	$CDCl_3$
$RuL(CO)Cl_2(DMF)$	2.73, 2.89 (DMF 2.98, 3.06)	Me_2SO d_6	*b*	
$RuL_2(CO)Cl^+$	1.64, 1.84 3.43 3.46	CD_3CN	20.41, 22.99, 26.41, 27.66 (CO 202)	CD_3CN
$RuL_2(CH_3CN)_2^+$	1.73, 3.13 (CH_3CN 2.38)	CD_3CN	23.41, 26.64, (CH_3CN 4.73)	Me_2SO-d_6
RuL_2Cl_2	2.41, 2.87	CD_2Cl_2	*b*	
$RuL_2(H_2O)_2^{2+}$	1.83, 2.64	D_2O	25.17	D_2O
$RuL_2(CN)_2$	1.76, 3.53	$CD_3OD + CDCl_3$	*b*	
L′	2.88	$CDCl_3$	25.8	$CDCl_3$
$RuL'_2(H_2O)_2^{2+}$	1.53, 2.53	D_2O	*b*	
$RuL'_2(CH_3CN)_2^{2+}$	1.71, 3.29 (CH_3CN 2.19)	CD_3CN	24.45, 27.55 (CH_3CN 4.54)	CD_3CN

[a] Me_4Si was used as an internal reference. [b] Accurate ^{13}C NMR spectra were not obtained due to the too low solubility of the complexes.

Table V. Electrochemical Properties: $E_{1/2}$ Values Determined by Cyclic Voltammetry for the 6,6′-dmbp (L) and 2,9-dmp (L′) Ruthenium Complexes[a]

	E, V vs. SCE (ΔE_p, mV)					
complex	II/III	III/IV	IV/V	V/VI	electrode	solvent
$RuL(CO)Cl_2(DMF)$	1.40 (70)				Pt	CH_3CN
$RuL_2(CO)Cl^+$	1.60 (60)				Pt	CH_3CN
$RuL_2(CH_3CN)_2^{2+}$[b]	1.50 (60)				Pt	CH_3CN
$RuL_2(OH_2)_2^{2+}$	0.72 (60)	0.87 (80)	1.10 (100) ($I_{p_a} >> I_{p_c}$)	$E_{p_a} = 1.45$ (irr)	CV (activated)	H_2O (0.1 N CF_3SO_3H)
cis-$Ru(bpy)_2(H_2O)_2^{2+}$[32]	0.65	0.93	1.10	1.23	CV	H_2O (pH 1.5)
trans-$Ru(bpy)_2(H_2O)_2^{2+}$[32]	0.45	1.01			CV	H_2O (pH 1.5)
$RuL'_2(H_2O)_2^{2+}$	0.72 (65)		1.06 (100) ($I_{p_a} >> I_{p_c}$)	$E_{p_a} = 1.42$ (irr)	CV	H_2O (1 N HBF_4)
$RuL'_2(CH_3CN)_2^{2+}$[b]	1.45 (70)				Pt	CH_3CN

[a] For experimental conditions, see Experimental Section; scan rate = 100 mV s^{-1}. [b] $RuL_2(CH_3CN)_2^{2+}$ and $RuL'_2(CH_3CN)_2^{2+}$ show reversible Ru^{II}/Ru^I and Ru^I/Ru^0 couples at −1.4 and −1.6 V (ΔE_p = 60 mV); the other complexes studied are irreversibly reduced below −1.4 V.

of the diimine ligand once coordinated. Interestingly, the two diaquo complexes show markedly separate signals for the two methyl groups of each chelate, the difference of their chemical shifts being ~1 ppm.

In addition, the line widths, $\Delta\nu_{1/2}$, of the various peaks are noticeably different, tending to indicate that the dynamic properties of the two methyl groups are not identical. According to the hypothetical structure represented in Figure 2 and in agreement with CPK models, the most shielded CH_3's are likely to be those at the back (see Figure 2); indeed, due to the important ring current effect of the bpy or phen nuclei, the methyl groups close to these rings are expected to be shielded. Due to the large steric interaction between these CH_3's and the bpy or phen nuclei, broadening of their corresponding signals, as shown in Figure 3, is not unexpected. The two low-field methyl groups are highly sensitive to the nature of the other ligands, as expected from the geometry of the molecule (see Figure 2).

In the case of $Ru(6,6'\text{-dmbp})_2(CO)Cl^+$, the C_2 symmetry axis is lost; each pyridinic ring becomes different from the others and four CH_3 peaks are observed. ^{13}C NMR spectra confirm the hypothetical structures of the various complexes synthesized. Surprisingly, $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ shows only one CH_3 peak (δ = 25.17).

(3) Electrochemical Properties. The redox potentials of the various couples are indicated in Table V. As an example, the cyclic voltammograms of two representative bis(6,6′-dimethyl-2,2′-bipyridine) complexes are shown in Figure 4. For the bis(diimine) complexes containing CO or CH_3CN, the measured values are higher than 1.4 V vs. SCE. These anodic potentials show that the +2 oxidation state of Ru is stabilized by strong acceptor ligands. On the other hand, H_2O as an ancillary ligand greatly stabilizes the +3 oxidation state, as compared to CH_3CN: $E_{1/2}$ (Ru^{III}/Ru^{II}) is almost 0.8 V more anodic for $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2^{2+}$ than for the diaquo analogue, $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$.

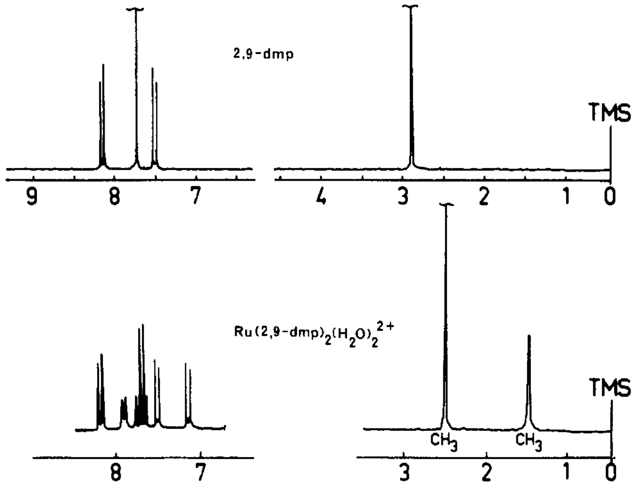

Figure 3. ^1H NMR spectra (200 MHz) of 2,9-dmp ($CDCl_3$) and $Ru(2,9\text{-dmp})_2$ $(H_2O)_2^{2+}$ (heavy water).

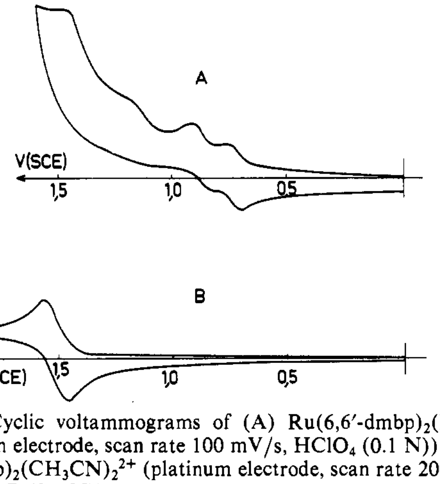

Figure 4. Cyclic voltammograms of (A) $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ (glassy-carbon electrode, scan rate 100 mV/s, $HClO_4$ (0.1 N)) and (B) $Ru(6,6'\text{-dmbp})_2(CH_3CN)_2^{2+}$ (platinum electrode, scan rate 200 mV/s, CH_3CN–TEAP (0.1 N)).

Redox processes involving high oxidation states are more easily observed on activated vitreous carbon than on platinum, as previously shown for *cis*-$Ru(bpy)_2(H_2O)_2^{2+}$.[32] In the case of $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$, oxidation and reduction peaks, corresponding to redox processes involving the III/IV, IV/V, and V/VI couples, were obtained. The stabilization of high oxidation states

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Table VI. Oxidation of Water by Cerium(IV), Catalyzed by Mono- and Dinuclear Ruthenium Complexes

run	catalytic species	O_2 yield[a]	turnover no. on Ru complex[b]	medium (0.1 N)	observn
1	$RuCl_3 \cdot 3H_2O$	0		$HClO_4$	formation of a black deposit of RuO_2
2	RuO_2 (Ventron)	8		$HClO_4$	same as run 1
3	$RuL_2(H_2O)_2^{2+}$	0		$HClO_4$	homogeneous solution throughouth the experiment
4	$RuL_2(H_2O)_2^{2+}$	0		H_2SO_4	same as run 3
5	$Ru(bpy)_2CO_3$	~0		H_2SO_4	same as run 1
6	$Ru(bpy)_2Cl_2$	16		$HClO_4$	same as run 3
7	$(Ru{-}O{-}Ru)^{4+}$[c]	60	13.2	$HClO_4$	formation of a brown cristalline solid (not RuO_2)
8	$(Ru{-}O{-}Ru)^{4+}$[c,d]	25	4.7	$HClO_4$	same as run 7
9	$(Ru{-}O{-}Ru)^{4+}$[c]	30	2.2	$HClO_4$	same as run 7
10	$(Ru{-}O{-}Ru)^{4+}$[c]	87	6.6	CF_3SO_3H	same as run 3

[a] Calculated with respect to cerium(IV): yield = 100(mol of O_2 produced)/4(mol of cerium(IV) introduced). [b] Determined as the ratio of mol of O_2 produced/mol of ruthenium complex used. [c] $(Ru{-}O{-}Ru)^{4+} = [(bpy)_2(H_2O)RuORu(bpy)_2(H_2O)]^{4+}(ClO_4^-)_4$. [d] Addition of fresh cerium(IV) solution at the end of run 7.

of ruthenium, on the time scale of the cyclic voltammetry method, is made possible by simultaneous exchange of protons and electrons,[8] according to the possible following reactions:

$$Ru^{II}L_2(OH_2)_2^{2+} \underset{H^+,\ e^-}{\overset{-H^+,\ -e^-}{\rightleftarrows}} Ru^{III}L_2(H_2O)(OH)^{2+} \underset{H^+,\ e^-}{\overset{-H^+,\ -e^-}{\rightleftarrows}}$$

$$Ru^{IV}L_2(O)(OH_2)^{2+} \underset{H^+,\ e^-}{\overset{-H^+,\ e^-}{\rightleftarrows}} Ru^{V}L_2(O)(OH)^{2+} \underset{H^+,\ e^-}{\overset{-H^+,\ -e^-}{\rightleftarrows}}$$

$$Ru^{VI}L_2(O)_2^{2+}$$

$$L = 6,6'\text{-dmbp or } 2,9\text{-dmp}$$

Linear dependence of the redox potentials with pH is indeed observed in acidic medium (pH <3). However, these electrochemical steps are not easily observed individually,[33] the difficulties being mainly due to adsorption phenomena or precipitation on the electrodes, slow electrochemical kinetics, simultaneous multiproton exchange, etc. Electrolysis at fixed potential (+0.8 V vs. SCE) in aqueous H_2SO_4 (2 N) and a spectrophotometric titration of $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ by cerium(IV) show that the first oxidation step indeed corresponds to the conversion of the +2 state to the +3 oxidation state. The green solution of ruthenium(III) thus obtained is only moderately stable. After a few hours at room temperature, the solution contains an important fraction of the starting species, $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$, as indicated by optical measurements. In addition, this reaction is accelerated by daylight. The processes involved in the reduction, with regeneration of some of the starting ruthenium(II) complex, are not clear. It might be envisaged that a disproportionation reaction of the ruthenium(III) complex occurs:

$$2Ru^{III}(6,6'\text{-dmbp})_2(H_2O)(OH)^{2+} \rightarrow$$
$$Ru^{II}(6,6'\text{-dmbp})_2(H_2O)_2^{2+} + Ru^{IV}(6,6'\text{-dmbp})_2(O)(H_2O)^{2+}$$

Such a scheme has been proposed to explain the reactivity of $Ru^{III}(bpy)_2(py)(H_2O)^{3+}$ (py = pyridine).[33] Recently, it was supposed that a chemical step, corresponding to ligand exchange accompanied by cleavage of a ruthenium to nitrogen bond, was also involved in the case of $Ru(terpy)(bpy)(H_2O)^{3+}$ (terpy = 2,2′,6′,6″-terpyridine).[34] Obviously oxidative degradation of the organic ligands may also take place.

(4) Attempts To Oxidize H_2O to O_2: Involvement of Dinuclear Complexes of Ruthenium in the Reaction of O_2 Formation. Polypyridinic complexes of ruthenium have been used in homogeneous catalysis and electrocatalysis, for instance, they have shown interesting catalytic properties in oxidation of various organic substrates[8,35,36] (alcohols, aldehydes, or hydrocarbons). A particularly interesting feature of these complexes is their ability to catalyze multielectronic processes involved in the reductive or oxidative transformation of inorganic species; for instance, $Ru(bpy)_2py(H_2O)^{2+}$ is a good electrocatalyst for nitrate reduction,[22] whereas Cl^- electrooxidation is greatly facilitated in the presence of bis(bipyridine)ruthenium complexes.[7,37]

Using the presently reported complexes, we have mainly focused our studies on water oxidation to molecular oxygen. In order to test potentially catalytic systems, one of the most convenient reactions is cerium(IV) reduction in acidic medium ($E°(Ce^{IV}/Ce^{III}) = 1.44$ V vs. NHE). The amount of O_2 formed according to the reaction

$$4Ce^{IV} + 2H_2O \rightarrow 4Ce^{III} + O_2 + 4H^+$$

has been measured by both amperometric and chromatographic methods. From the results obtained, the most important conclusion that can be drawn is the following: neither $Ru(6,6'\text{-dmbp})_2(H_2O)_2^{2+}$ nor $Ru(2,9\text{-dmp})_2(H_2O)_2^{2+}$ leads to water oxidation, whereas the dinuclear complex $(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2^{4+}$, earlier studied by Meyer et al.,[7] is a good catalyst of O_2 formation from water and cerium(IV).

Some experimental data on catalytic oxidation of water are listed in Table VI. Indeed, with our bis(diimine) complexes, no trace of O_2 could be detected, even by means of the very sensitive method based on an oxygen electrode. At the same time, these complexes seem to be chemically resistant, even under acidic and oxidizing conditions, since no ruthenium oxide deposit could be seen after the run. Clearly no intermediate RuO_4 was formed, in contrast to reactions with $Ru(bpy)_2(H_2O)_2^{2+}$. With the latter, small amounts of O_2 were formed but, at the same time, a black deposit characteristic of RuO_2 was obtained. Bis(bipyridine) complexes of ruthenium display contradictory behavior, depending on their precursor. $Ru(bpy)_2CO_3$, dissolved in 0.1 N H_2SO_4 at room temperature, turns out to be an extremely poor catalyst, whereas *cis*-$Ru(bpy)_2Cl_2$, hydrolyzed at 60 °C in 0.1 M $HClO_4$ shows noticeably activity, catalyzing O_2 formation from H_2O and Ce^{IV} with a 16% yield. In fact, the dissimilarity between the two complexes is only apparent: $Ru(bpy)_2CO_3$ leads only to $Ru(bpy)_2(H_2O)_2^{2+}$ under the mild hydrolysis conditions used, but when *cis*-$Ru(bpy)_2Cl_2$ is heated in perchlorate medium, a small fraction of this complex is converted to the dinuclear species $(bpy)_2(H_2O)RuORu(bpy)_2H_2O^{4+}$. Indeed, such a transformation is easily monitored by visible spectroscopy, due to the characteristic band of the μ-oxo dimer.[7]

We have confirmed that the dinuclear oxo complex of ruthenium is indeed an efficient catalyst for water oxidation to O_2 (see Table V). Even the most reliable method of analysis, based on direct measurements of oxygen gas quantities by vapor-phase chromatography, leads to particularly spectacular results. For instance, the oxidizing power of Ce^{IV} gives an 87% yield of O_2 under certain conditions (CF_3SO_3H 0.1 M; pH 1.0), the overall turnover number on the (μ-oxo)ruthenium dimer being 6.6 mol of O_2/mol of ruthenium at the end of the experiment. According to our data (see Table V), it appears that mononuclear ruthenium species are unable to promote water oxidation. When hindered complexes are used, whose transformation to dinuclear species seems to be very unlikely for steric reasons, no O_2 is formed (runs 3 and 4). On the other hand, if one starts with $(bpy)_2(OH_2)$-

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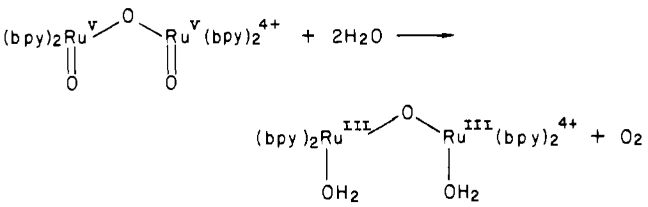
$RuORu(OH)_2(bpy)_2^{4+}$ or its mononuclear precursor, large amounts of O_2 can be obtained (runs 6–10), with the catalytic process probably occuring on two sites, with simultaneous exchange of protons and electrons, as earlier postulated:[7]



Finally, the experimental results of homogeneous catalysis of water oxidation by ruthenium complexes must be regarded with great caution. The decomposition products of the compounds are often ruthenium oxides, and thus they are likely to be catalytically active.[38,39] Knowing how difficult it is to definitely prove that a reacting medium remains homogeneous, one should exercise great care when drawing conclusions.

Conclusion

Several complexes of ruthenium(II), containing two molecules of sterically hindering diimine as ligands, have been prepared and characterized. None of these complexes display catalytic activity for O_2 formation from water, in the presence of excess cerium(IV). In these compounds, the presence of methyl substituents prevents condensation to μ-oxo polynuclear ruthenium complexes. On the contrary, the dinuclear complex $(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2^{4+}$ acts as an efficient catalyst. With this compound, up to 13.2 mol of O_2/mol of μ-oxo complex have been obtained. It seems therefore clear that a multimetallic system is required to promote water oxidation to oxygen, in analogy with the postulated mechanism of the manganese-containing enzyme of photosystem II in natural photosynthesis.[3]

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Registry No. $RuL(CO)Cl_2(DMF)$, 99547-13-4; $[RuL_2(CO)Cl](ClO_4)$, 99547-15-6; $[RuL_2(CH_3CN)_2](ClO_4)_2$, 99547-17-8; RuL_2Cl_2, 99547-18-9; $[RuL_2(H_2O)_2](ClO_4)_2$, 99547-20-3; $RuL_2(CN)_2$, 99547-21-4; $[RuL'_2(CH_3CN)_2](ClO_4)_2$, 99547-23-6; RuL'_2Cl_2, 99547-24-7; $[RuL'_2(H_2O)_2](ClO_4)_2$, 99547-26-9; $[RuL(CO)Cl_2(DMF)]^+$, 99547-27-0; $[RuL_2(CO)Cl]^{2+}$, 99547-28-1; $[RuL_2(CH_3CN)_2]^{3+}$, 99547-29-2; $[RuL_2(H_2O)_2]^{3+}$, 99547-30-5; $[RuL'_2(H_2O)_2]^{3+}$, 99547-31-6; $[RuL'_2(CH_3CN)_2]^{3+}$, 99547-32-7; $[RuL_2(H_2O)_2]^{4+}$, 99547-33-8; $[RuL_2(H_2O)_2]^{5+}$, 99547-34-9; $[RuL_2(H_2O)_2]^{6+}$, 99547-35-0; $[RuL'_2(H_2O)_2]^{5+}$, 99547-36-1; $[RuL'_2(H_2O)_2]^{6+}$, 99547-31-6; $[RuL_2(CH_3CN)_2]^+$, 99559-71-4; $[RuL'_2(CH_3CN)_2]^+$, 99547-32-7; $RuL_2(CH_3CN)_2$, 99547-37-2; $RuL'_2(CH_3CN)_2$, 99547-38-3; H_2O, 7732-18-5; $RuCl_3$, 10049-08-8; RuO_2, 12036-10-1; $Ru(bpy)_2CO_3$, 59460-48-9; $Ru(bpy)_2Cl_2$, 19542-80-4; $[Ru\text{-}O\text{-}Ru](ClO_4)_2$, 56110-88-4.

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Cobalt(II) Chelate Catalyzed Oxidation of 3,5-Di-*tert*-butylcatechol

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Co(II) chelate catalyzed oxidation of 3,5-di-*tert*-butylcatechol (3,5-DtBC) has been studied in the nonaqueous phase under O_2 atmosphere at room temperature. The only oxidation product is a corresponding *o*-benzoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ), irrespective of the Co(II) chelate catalyst used. The following overall stoichiometric equation without H_2O_2 accumulation is suggested for the $Co^{II}(acac)_2$ catalyzed oxidation of 3,5-DtBC by O_2 absorption measurements and analysis of the oxidation product and H_2O_2: 3,5-DtBC + $^1/_2O_2$ → 3,5-DtBQ + H_2O. Variation in cobalt(II) chelates is found to appreciably affect the catalytic activity in 3,5-DtBC oxidation. The effect of the addition of amine on the oxidation activity is discussed in connection with the behavior of the electronic absorption spectra of the cobalt–amine catalytic systems. By observation of the catalytic activity of Co(II) chelate–pyridine derivative systems, the importance of the affinity of the Co(II) chelate toward the oxygen molecule is suggested. The rate of $Co^{II}(acac)_2$ catalyzed oxidation is found to be first order with respect to the concentrations of $Co^{II}(acac)_2$ and 3,5-DtBC, respectively, and also first order in the partial pressure of molecular oxygen. The kinetic parameters for the 3,5-DtBC oxidation are estimated in the temperature range 286–309 K. A reaction scheme is proposed to account for these results. It involves the reaction of a $Co^{II}(acac)_2$–3,5-DtBC complex with O_2 to give a ternary 3,5-DtBC–Co^{II}–O_2 complex and the intramolecular reaction of the ternary oxygenated Co complex to give 3,5-DtBQ in the rate-determining step.

Introduction

Liquid-phase oxidation of catechol and its derivatives catalyzed by metal complexes has been the subject of considerable interest in recent years. A variety of metal complexes, e.g. Cu(II),[1-6] Fe(III),[7-13] Ru(II),[14] and V(IV)[15] complexes, that effect the oxidative cleavage of catechol have been reported. Oxidases or enzymes catalyzing reactions of oxygen are a particularly intriguing area in the field of reaction mechanisms. Some of the most interesting oxidases are in the group exemplified by the enzyme pyrocatechase, in which entire oxygen molecules are incorporated into an enzyme molecule in what appears to be a single reaction.[16] The metal ion catalyzed oxidation of 3,5-di-*tert*-butylcatechol by

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