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Synthesis, physicochemical and electrochemical properties of metal–metal bonded ruthenium corrole homodimers

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Abstract

Two diruthenium(III,III) corrole dimers, $[(Et_6Me_2Cor)Ru]_2$ and $[(Me_6Et_2Cor)Ru]_2$, where Et_6Me_2Cor and Me_6Et_2Cor are the 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole and 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole trianions, respectively, were synthesized and characterized as to their spectroscopic and electrochemical properties. They exhibit up to three oxidations and two reductions by cyclic voltammetry in CH_2Cl_2 or pyridine containing 0.1 M TBAP, almost all of which are electrochemically reversible on the voltammetric and/or thin-layer spectroelectrochemical timescale. The two reductions and the first two oxidations involve one-electron transfer processes which are separated from each other by 770–880 mV upon reduction and by 350–420 mV upon oxidation. The UV–vis spectroelectrochemical data suggest that the first two one-electron oxidations occur at the diruthenium metal centers while the third oxidation (seen only in CH_2Cl_2) is proposed to be macrocycle-based, leading to the formation of a $Ru_2(IV,IV)$ corrole species. The formation of a $Ru(III,IV)$ complex after abstraction of one electron is also suggested by the rhombic ESR spectrum of singly oxidized $[(Me_6Et_2Cor)Ru]_2$ at 77 K. The first one-electron reduction is also assigned as metal-centered and leads to the formation of a $Ru_2(III,II)$ complex. Finally, a comparison of electrochemical properties between the investigated diruthenium(III,III) corroles and an earlier characterized diruthenium(II,II) octaethylporphyrin, $[(OEP)Ru]_2$, is presented. © 2002 Published by Elsevier Science B.V.

Keywords: Ruthenium corrole homodimers; UV–vis spectroelectrochemical data; Physicochemical and electrochemical properties

1. Introduction

Corroles have in recent years attracted increasing attention as to their chemical and physicochemical properties. This has been due in large part to the improved synthesis of stable free-base corroles containing different alkyl or aryl substituents on the macrocycle which has, in turn, led to an increased activity in the preparation and characterization of metallocorroles in different metal oxidation states. Indeed, more than 20 different transition or main group metal ions have to date been inserted into the cavity of a corrole macrocycle [1,2]. These compounds can coordinate a variety of different axial ligands and have been characterized with nitrogen, oxygen, halogen or carbon donor ligands [1].

Despite recent advances in the field of corrole synthesis, the organometallic chemistry of these compounds is far less developed than in the case of porphyrins and until recently, no metal–metal bonded corrole derivative had been reported in the literature. Our laboratories have long been interested in porphyrins containing metal–carbon and metal–metal bonds [3,4] and we therefore turned our attention to the synthesis and characterization of similar derivatives in the corrole series. We wished to prepare and isolate metal–metal bonded corroles in high oxidation states and chose as one of our first examples, the ruthenium derivatives which are well-known in the porphyrin literature and exemplified by $[(OEP)Ru]_2$ where OEP is the dianion of octaethylporphyrin [5,6].

The first attempt to insert a ruthenium atom into a corrole macrocycle was reported by Boschi et al. in 1990 [7]. The attempted metalation reaction was carried out

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in dimethylformamide using ruthenium trichloride as a metalating agent but led directly to the formation of a metalloporphyrin rather than to a metalocorrole. The authors postulated that a carbonyl group was inserted from the solvent into the pyrrole–pyrrole bond of the corrole ring, thus leading to the corresponding porphyrin. The formation of a metalloporphyrin rather than a metalocorrole also occurred when trisruthenium dodecacarbonyl and toluene were used [7].

Our own attempts to insert a ruthenium ion into the macrocyclic cavity of a corrole was first performed using ruthenium trichloride as a metalating agent and high boiling solvents which were free from carbonyl groups, i.e. pyridine, xylene, benzonitrile and trichlorobenzene. Unfortunately, a significant degradation of the corrole ring occurred in these solvents at high temperature and no trace of the metalated corrole or porphyrin was detected.

Finally, we showed in a preliminary communication that the diruthenium corrole could be synthesized using as metalating agent the μ -dichloro-(1,5-cyclooctadiene)ruthenium dimer, $[(\text{COD})\text{RuCl}_2]_2$. The gentle reaction of $[(\text{COD})\text{RuCl}_2]_2$ [8,9] with $(\text{Et}_6\text{Me}_2\text{Cor})\text{H}_3$ directly afforded the metal–metal bonded dimer, $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ [10]. The structure of this latter derivative exhibits the two direct pyrrole bonds staggered by 180° with respect to each other. $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ is the first example of a ruthenium corrole as well as the first metal–metal bonded derivative to be synthesized in the corrole series. We now report the synthesis of a second structurally similar diruthenium corrole, $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$, as well as give a full spectroscopic and electrochemical characterization of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ and $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ where $\text{Et}_6\text{Me}_2\text{Cor}$ and $\text{Me}_6\text{Et}_2\text{Cor}$ represent the trianions of 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole and 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole respectively. Both compounds can exist in six different oxidation states, four of which were spectroscopically characterized.

2. Experimental

2.1. Instrumentation

$^1\text{H-NMR}$ spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Microanalyses were performed at the Université de Bourgogne on a Fisons EA 1108 CHNS instrument. UV–vis spectra were recorded on a Varian Cary 5E spectrophotometer. ESR experiments were performed on a Bruker or IBM Model ESP 300 spectrometers. Mass spectra were obtained in linear mode with a Bruker Proflex III MALDI/TOF mass

spectrometer using dithranol as matrix. Cyclic voltammetry was carried out with an EG&G model 173 potentiostat. A three-electrode system was used and consisted of a glassy carbon or platinum disk-working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

UV–vis spectroelectrochemical experiments were performed with an optically transparent platinum thin-layer electrode of the type described in the literature [11]. Potentials were applied with an EG&G model 173 potentiostat. Time-resolved UV–vis spectra were recorded with a Hewlett Packard Model 8453 diode array rapid-scanning spectrophotometer.

2.2. Chemicals and reagents

Absolute dichloromethane (CH_2Cl_2) and pyridine (py) were obtained from Fluka Chemical Co. and used as received. tetra-*n*-Butylammonium perchlorate (TBAP, Fluka Chemical Co.) was twice recrystallized from absolute ethanol and dried in a vacuum oven at 40°C for a week. 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole ($\text{Et}_6\text{Me}_2\text{Cor})\text{H}_3$ and 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole ($\text{Me}_6\text{Et}_2\text{Cor})\text{H}_3$ were prepared as described previously [12,13].

2.2.1. bis- μ -Dichloro(1,5-cyclooctadiene)ruthenium(II)

$[(\text{COD})\text{RuCl}_2]_2$ was prepared as described in the literature [14].

2.2.2. bis[Ruthenium(III)-(8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole)], $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$

8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole (0.2 g, 0.46 mmol) and dichloro(1,5-cyclooctadiene)ruthenium(II) dimer (0.512 g, 0.91 mmol) were refluxed in a solution containing 40 ml of 2-methoxyethanol and 2 ml of triethylamine. After 20 min, the solvent was evaporated and the resulting solid dissolved in dichloromethane and then chromatographed on basic alumina (Merck 1097, grade III; eluent: CH_2Cl_2). The first eluting fraction was collected and evaporated. The solid was recrystallized from a $\text{CH}_2\text{Cl}_2 + \text{MeOH}$ mixture upon cooling to afford 0.126 g of the diruthenium(III) dimer, $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$, as black crystals (0.14 mmol, yield = 51%). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.65 (t, 12H, CH_2CH_3), 3.73 (s, 12H, CH_3), 3.88 (q, 8H, CH_2CH_3), 4.10 (s, 12H, CH_3), 4.53 (s, 12H, CH_3), 8.56 (s, 4H, CH), 8.76 (s, 2H, CH). MS m/z (%) = 1073 (100), 1074.31. Calc. for $\text{C}_{58}\text{H}_{62}\text{N}_8^{102}\text{Ru}_2$. UV–vis. (CH_2Cl_2): λ_{max} , nm (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) = 335 (88600), 395 (53300), 521 (1600). Calc. for $\text{C}_{58}\text{H}_{62}\text{N}_8\text{Ru}_2$: C, 64.90; H, 5.82; N, 10.44. Found: C, 64.67; H, 5.81; N, 10.47%.

2.2.3. bis[Ruthenium(III)-(2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole)]

[(Et₆Me₂Cor)Ru]₂ was synthesized as described in the literature [10]. ¹H-NMR (CDCl₃) δ (ppm): 1.64 (m, 12H, CH₂CH₃), 1.71 (s, 12H, CH₃), 1.74 (m, 12H, CH₂CH₃), 1.87 (m, 12H, CH₂CH₃), 3.65 (m, 8H, CH₂CH₃), 3.83 (q, 8H, CH₂CH₃), 3.95 (m, 8H, CH₂CH₃), 8.56 (s, 4H, CH), 8.76 (s, 2H, CH). MS *m/z* (%) = 1185 (100), 1186.45 Calc. for C₆₆H₇₈N₈¹⁰²Ru₂. UV–vis. (CH₂Cl₂): λ_{max}, nm (ε, 1 mol⁻¹ cm⁻¹) = 336 (103300), 393 (59100), 521 (1600). Calc. for C₅₈H₆₂N₈Ru₂: C, 66.87; H, 6.63; N, 9.45. Found: C, 66.93; H, 6.69; N, 9.50%.

3. Results and discussion

3.1. Synthesis

[(COD)RuCl₂]₂ was obtained by reaction of ruthenium trichloride with 1,5-cyclooctadiene in ethanol. The synthesis of the dimer involves a redox reaction between RuCl₃ and ethanol. After 12 h of reaction, [(COD)RuCl₂]₂ was quantitatively obtained as a fine brown powder precipitate.

When [(COD)RuCl₂]₂ and (Me₆Et₂Cor)H₃ in 2-methoxyethanol were refluxed for 20 minutes, the UV–vis spectrum of the solution indicated a complete metalation of the macrocycle. The presence of triethylamine is required to trap HCl molecules released during the reaction. In the absence of triethylamine, the NH groups of the corrole are protonated and the reaction stops. The reaction was carried out in the open air in order to enhance the oxidation of Ru(II) to Ru(III) needed to form [(Me₆Et₂Cor)Ru]₂ (Scheme 1).

The mass spectral and UV–vis absorption data confirm synthesis of the dimer after insertion of ruthenium inside the macrocyclic cavity.

3.2. Spectroscopic characterization

Upon metalation of (Me₆Et₂Cor)H₃, the free-base corrole Q bands located between 550 and 600 nm disappear. At the same time, the Soret band of the free-base corrole undergoes a strong hypsochromic shift and moves from 396 to 335 nm (shoulder at 395 nm) for the binuclear complex (see Section 2). As is seen in the case of covalently linked Co(III) bis-corroles [15], the

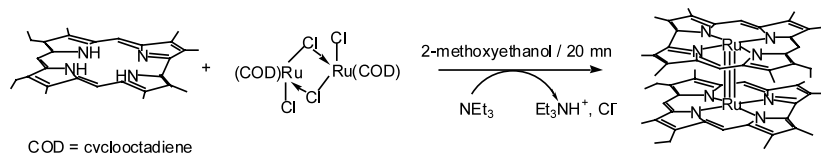
close proximity of both macrocycles to each other is associated with a strong electronic interaction between the π systems of each macrocycle. This interaction is associated with changes in the UV–vis spectrum of the complex; the stronger the interaction, the larger is the blue shift of the Soret band from the simple mononuclear complex. A similar blue shift of the Soret band is observed for [(Et₆Me₂Cor)Ru]₂ (see Section 2).

The mass spectral data confirm the structure of the diruthenium(III,III) complex by indicating a pattern with the largest peak centered at *m/z* = 1073. There is no evidence in the mass spectrum for the presence of ruthenium corrole monomer whose molecular ion would be localized around 537 nm in the absence of any axial ligands (see Section 2).

The ruthenium atom has many isotopes: ⁹⁶Ru, ⁹⁸Ru, ⁹⁹Ru, ¹⁰⁰Ru, ¹⁰¹Ru, ¹⁰²Ru, ¹⁰⁴Ru. Consequently, the isotopic cluster is complex and exhibits many peaks. A simulation of the molecular ion shows perfect agreement between the experimental and theoretical isotopic clusters. However, due to the high vacuum inside the mass spectrometer, the formation of a dimeric species from the monomer during analysis cannot be unambiguously excluded.

The ruthenium(III) atom has five valence electrons distributed in the five d orbitals. This odd number of electrons implies that ruthenium(III) is paramagnetic. Therefore, the presence of a ruthenium(III) monomer should be detected by both ¹H-NMR and ESR spectroscopies. Conversely, a metal–metal bonded Ru(III) dimer would have ten d electrons (2 × 5) and according to the qualitative orbital diagram developed by Cotton and coworkers [16,17], would be diamagnetic with a Ru–Ru bond order of 3. The absence of an ESR signal for the investigated corroles at 100 K in toluene confirms the lack of any paramagnetic compound and therefore the presence of only a Ru₂(III,III) dimer. This result also demonstrates that formation of a ruthenium corrole monomer is not favorable under the given experimental conditions.

The ¹H-NMR spectra of the compounds are in agreement with results from the ESR measurements. Indeed, all of the NMR signals are localized in a ‘diamagnetic’ region of the spectrum, ranging between 1.50 and 9.00 ppm (see Section 2). No other signals are detected outside of this area, thus confirming the selective formation of the diruthenium species.



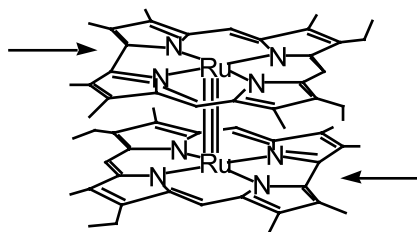
Scheme 1.

An analysis of the $^1\text{H-NMR}$ spectra indicates that the structure of $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ is probably the same as that of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ which was structurally characterized in a preliminary communication [10].

Similar chemical shifts are observed for the protons of the two dimers. It is noteworthy to point out that the *meso* protons of $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ appear as two singlets of 2/1 intensity at 8.56 and 8.76 ppm (Scheme 2); these protons are shifted upfield by ca. 1.5 ppm when compared to a reference diamagnetic corrole monomer, $[\text{Me}_8\text{Cor}]\text{In}$ where Me_8Cor is the trianion of 2,3,7,8,12,13,17,18-octamethylcorrole [18]. This shift originates from the strong influence of both macrocycles which are maintained in close proximity to each other by the metal–metal triple bond. Similar behavior was previously observed for metal–metal bonded porphyrin dimers and double-decker complexes [19,20].

3.3. Electrochemical, spectroelectrochemical and ESR characterization

The electrochemistry of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ and $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ was investigated in CH_2Cl_2 and pyridine containing 0.1 M TBAP at room temperature and, in the case of CH_2Cl_2 , at -75°C . The half-wave potentials are summarized in Table 1 while the cyclic voltammograms are shown in Figs. 1 and 2.



mesoH : relative intensity: 2/1

Scheme 2.

Table 1

Half-wave potentials of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$, $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ and $[(\text{OEP})\text{Ru}]_2$ in CH_2Cl_2 or pyridine containing 0.1 M TBAP

Compound	Solvent	Oxidation				Reduction	
		4th	3rd	2nd	1st	1st	2nd
$[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}^{\text{III}}]_2$	py	–	–	0.55	0.20	–1.11	–1.88
$[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}^{\text{III}}]_2$		–	–	0.55	0.19	–1.11	–1.88
$[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}^{\text{III}}]_2$	CH_2Cl_2	1.14 ^b	1.14 ^b	0.55	0.14	–1.14	–2.02 ^d
$[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}^{\text{III}}]_2$		1.13 ^{b,c}	1.13 ^{b,c}	0.55	0.13	–1.14	–2.00 ^d
$[(\text{OEP})\text{Ru}^{\text{II}}]_2$ ^a		1.22	1.03	0.50	–0.46	–1.32	–

^a Potentials (V vs. Ag/AgCl) in CH_2Cl_2 , 0.2 M TBAP. Taken from Ref. [24].

^b Two overlapping one-electron processes.

^c A small re-reduction peak at $E_{\text{pc}} = 0.94$ V can also be observed at a scan rate of 0.1 V s^{-1} (see Fig. 2).

^d Value obtained at -75°C .

Three oxidations are observed for both compounds in CH_2Cl_2 . The first two oxidations involve reversible one-electron abstractions which are located at $E_{1/2} = 0.14$ and 0.55 V for $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ and at 0.13 and 0.55 V for $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$. The third oxidation is located at $E_{1/2} = 1.14$ or 1.13 V and involves two overlapping one-electron transfer steps as evidenced by a doubling of the peak current as compared to the other processes. This global two-electron oxidation is reversible for $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ but an unknown chemical reaction follows the electron transfer of $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ from room temperature to -75°C (see Fig. 2). Only a single reversible one-electron reduction is seen for the two compounds in CH_2Cl_2 at room temperature but two well-defined reductions are observed at -75°C where the negative potential range of the solvent has been increased slightly at low temperature. This is shown in Figs. 1b and 2b. Two reversible one-electron oxidations and two reversible one-electron reductions can also be seen in pyridine at room temperature (see Table 1 and Fig. 1a) but the third oxidation occurs beyond the potential range of this solvent.

The UV–vis spectral changes upon reduction and oxidation of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ and $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ in CH_2Cl_2 containing 0.2 M TBAP were examined by thin-layer spectroelectrochemistry. Similar spectroelectrochemical data were obtained for the two compounds and these results are discussed below in the case of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$.

Neutral $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ in CH_2Cl_2 , 0.2 M TBAP exhibits a Soret band at 336, a shoulder at 393 nm and no major bands in the visible region of the spectrum. Only small spectral changes are observed upon the first and second one-electron oxidations in a thin-layer cell (see Fig. 3) and this is interpreted in terms of a metal centered electron transfer. The UV–vis spectral changes obtained upon the third oxidation of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ are shown in Fig. 3c. A comparison of these spectral changes with what is observed during the first two oxidations suggests that the overall two-electron oxidation is macrocycle-centered, leading to formation of a

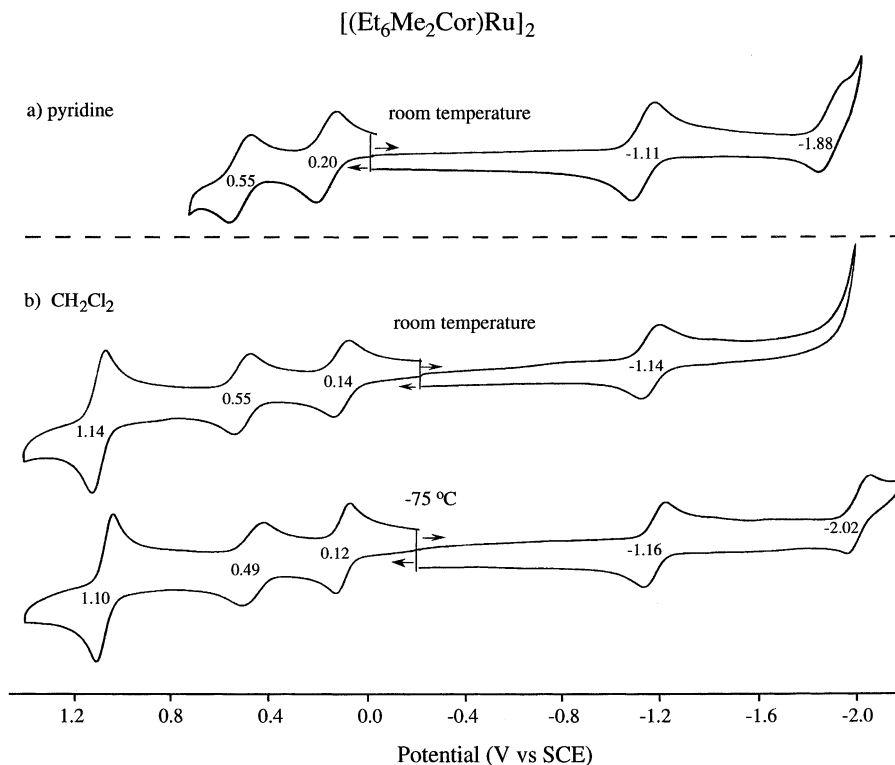


Fig. 1. Cyclic voltammograms of $[(Et_6Me_2Cor)Ru]_2$ (a) in pyridine, 0.1 M TBAP at room temperature and (b) in CH_2Cl_2 at room temperature and $-75\text{ }^\circ\text{C}$ containing 0.1 M TBAP.

$Ru_2(IV,IV)$ species which has two singly oxidized corrole rings.

Neutral $[(Et_6Me_2Cor)Ru]_2$ and $[(Me_6Et_2Cor)Ru]_2$ are ESR silent at temperatures down to 100 K indicating that the unpaired d electrons located on the two Ru(III) cores are coupled in the dimeric unit. Ruthenium(III,III)

compounds can exist with zero or two unpaired electrons. Magnetic susceptibility measurements were made on $[(Me_6Et_2Cor)Ru]_2$ using the Evan's method and indicate on $S = 0$ ground state at room temperature, consistent with the well-defined NMR spectrum characteristic of a diamagnetic species. An isotropic signal is

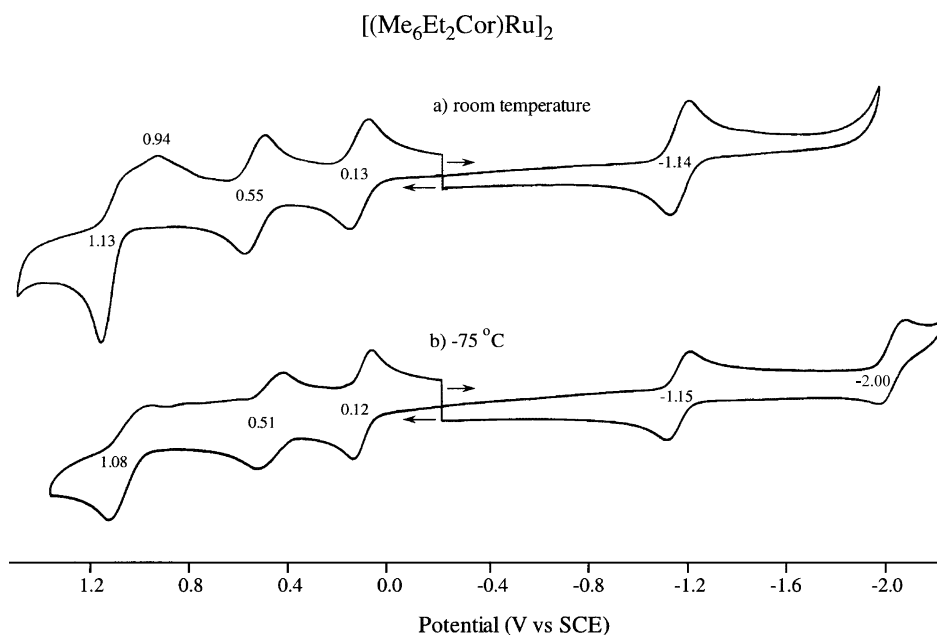


Fig. 2. Cyclic voltammograms of $[(Me_6Et_2Cor)Ru]_2$ in CH_2Cl_2 containing 0.1 M TBAP at (a) room temperature and (b) $-75\text{ }^\circ\text{C}$.

observed for both singly oxidized dimers at temperatures down to 100 K (see Fig. 4a for the case of $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2^+$) but the ESR spectrum of the same compound at 77 K (Fig. 4b) shows a rhombic g value pattern with $g = 2.049$, 1.991 and 1.928. This latter result is similar to that of other diruthenium compounds with $\text{Ru}_2(\text{III,IV})$ units [21,22] and clearly suggests a metal-centered oxidation, i.e. the formation of a $\text{Ru}_2(\text{III,IV})$ corrole under these experimental conditions.

The UV–vis spectral changes upon the first reduction of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ are given in Fig. 3d. The 336 nm band decreases in intensity and shifts to 320 nm while the 393 nm band increases in intensity as one electron is added to the dimer. The second reduction of the corrole dimers occurs at -1.88 V in pyridine and at close to -2.00 V in CH_2Cl_2 at low temperature. Definitive ESR could not be obtained to verify the site of the two reductions but these reactions are proposed to involve the metal center on the basis of known redox reactions for $\text{Ru}_2(\text{III,III})$ complexes [4,23] and comparisons with a related porphyrin dimer (see Section 3.4). The overall proposed electron transfer mechanism for the two investigated dimers is given in Scheme 3.

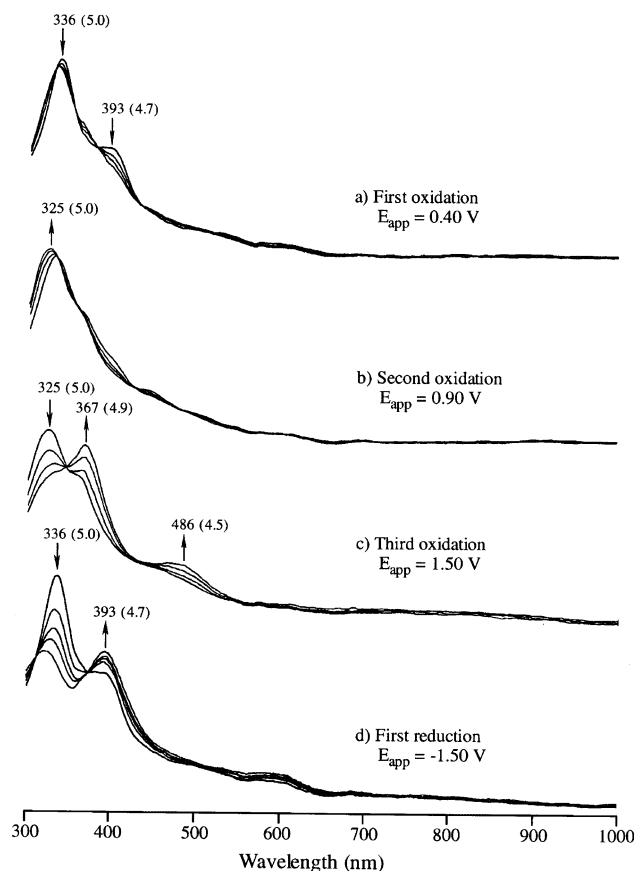


Fig. 3. Spectral changes of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ in CH_2Cl_2 containing 0.2 M TBAP obtained upon (a) the first oxidation at 0.40 V, (b) the second oxidation at 0.90 V, (c) the third oxidation at 1.50 V and (d) the first reduction at -1.50 V. The data in parenthesis are $\log \epsilon$.

3.4. Comparison between electrochemical behavior of corrole and porphyrin dimers

The metal–metal bonded ruthenium porphyrin dimer, $[(\text{OEP})\text{Ru}]_2$, where OEP = octaethylporphyrin dianion, was first synthesized by Hopf et al. [6] and later fully characterized by Collman et al. [5]. The compound undergoes four oxidations and one reduction in CH_2Cl_2 , all of which involve reversible one-electron transfers. The first two oxidations of $[(\text{OEP})\text{Ru}]_2$ were assigned as occurring at the dimetal center leading to the successive formation of dimers containing $\text{Ru}_2(\text{III,II})$ and $\text{Ru}_2(\text{III,III})$ units [24]. These reactions occur at $E_{1/2} = -0.46$ and 0.50 V versus Ag/AgCl in CH_2Cl_2 (see Table 1) and can be directly related to the same two metal-centered $\text{Ru}_2^{6+/5+}$ and $\text{Ru}_2^{5+/4+}$ processes of the corrole dimers which occur at -1.11 and -1.88 V in pyridine. Half-wave potentials for first and second electroreductions of $[(\text{Et}_6\text{Me}_2\text{Cor})\text{Ru}]_2$ and $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2$ (i.e. the $\text{Ru}_2(\text{III,III})$ and $\text{Ru}_2(\text{III,II})$ reductions) are sepa-

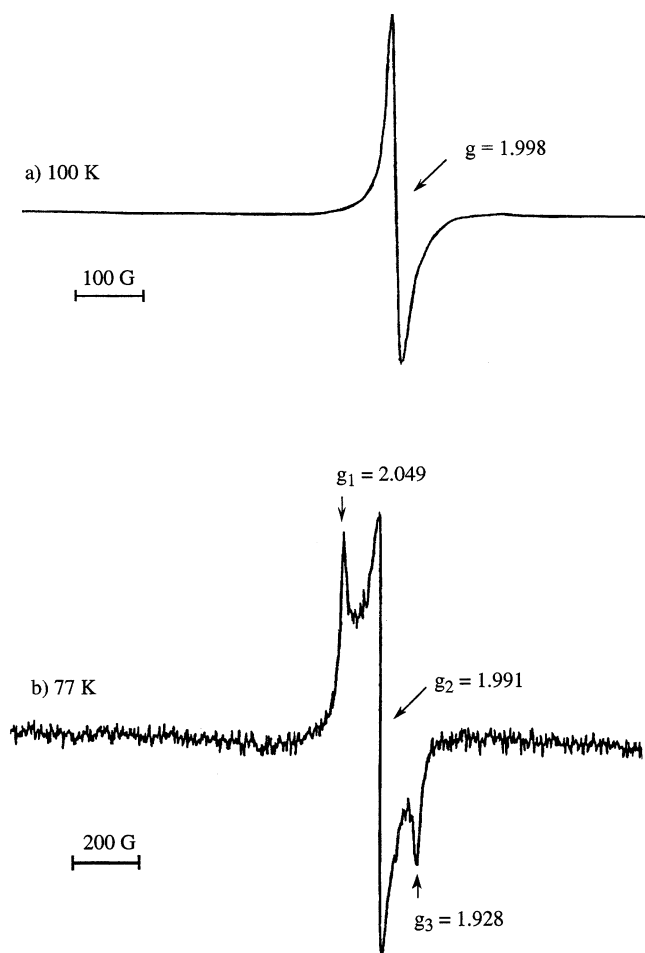
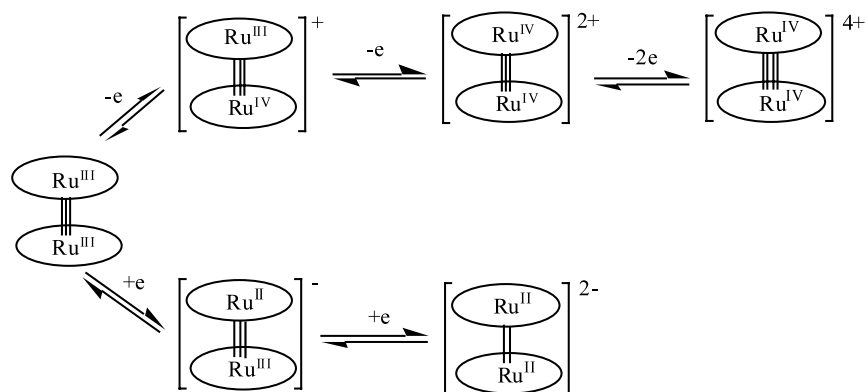


Fig. 4. ESR spectra of $[(\text{Me}_6\text{Et}_2\text{Cor})\text{Ru}]_2^+$ (a) at 100 K after chemical oxidation with AgClO_4 in toluene and (b) at 77 K after the controlled-potential oxidation at 0.45 V in CH_2Cl_2 containing 0.2 M TBAP.



rated by 0.77–0.88 V and these values are comparable to a separation in $E_{1/2}$ of 0.96 V between the same two metal-centered redox processes of [(OEP)Ru]₂.

The third and fourth oxidations of [(OEP)Ru]₂ occur at 1.03 and 1.22 V and were assigned as being ring-centered to generate the diruthenium(III,III) dication after a four-electron abstraction from the neutral complex. This contrasts with the case of [(Et₆Me₂-Cor)Ru^{III}]₂ and [(Me₆Et₂Cor)Ru^{III}]₂, both of which are proposed to undergo metal-centered oxidations which occur at 0.13–0.14 and 0.55 V versus SCE in CH₂Cl₂.

It has often been pointed out that the corrole macrocycle is able to stabilize metal ions in higher oxidation states than in the case of the corresponding porphyrins and this is indeed what is observed in the case of the diruthenium dimers. The two corrole dimers can be converted to a diruthenium(IV,IV) species after the abstraction of two electrons and this is followed by a Ru₂(IV,IV) dication at more positive potentials. In contrast, the previously investigated [(OEP)Ru]₂ complex is apparently not converted to its Ru₂(IV,IV) form but rather seems to be oxidized only to the Ru₂(III,III) dication and tetracation, [(OEP)Ru]₂²⁺ and [(OEP)Ru]₂⁴⁺, the latter of which has undergone an abstraction of two electrons from each of the two macrocycles. On the other extreme, the diruthenium porphyrin can be reduced to its diruthenium (II,I) form and this oxidation state is not accessible to the diruthenium corroles within the potential range of the electrochemically utilized solvents.

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