

Electrochemistry of Acetate-, Carbonate-, Sulfate-, and Dihydrogenphosphate-Bridged Dirhodium(II) Complexes

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Complexes, $[\text{Rh}_2(\text{B-B})_4\text{L}_2]^n$ ($\text{B-B} = \text{CH}_3\text{CO}_2^-$, $\text{L} = \text{CH}_3\text{CN}$, H_2O , Cl^- , Br^- , SCN^- ; $\text{B-B} = \text{CO}_3^{2-}$, SO_4^{2-} , H_2PO_4^- , $\text{L} = \text{H}_2\text{O}$, Cl^- , Br^- , SCN^-) were prepared and their cyclic voltammograms (CV) and electronic absorption spectra were measured in solution. The CV of the complexes exhibits a reversible one-electron transfer from a metal-based orbital. Constant potential electrolysis at the oxidation peak potential of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCCH}_3)_2]$ in acetonitrile yielded $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCCH}_3)_2]^+$, a mixed valent Rh(II)–Rh(III) cation complex. The formation of the mixed valent complex was monitored by measuring electronic absorption spectra of the solution *in situ* during the oxidative electrolysis. The reductive electrolysis of the mixed valent complex solution, in the same electrolysis cell, yielded the original electronic absorption spectrum of the starting complex. The changes in the oxidation and reduction potentials of the complexes with different axial ligands, $\text{L} = \text{H}_2\text{O}$, Cl^- , Br^- , SCN^- , are correlated to the relative energy changes of HOMO and LUMO of the complexes, which indicates the metal-axial ligand σ - and π -bonding interactions. Spectroscopic and CV data indicate that the degree of σ -interaction is $\text{Cl}^- > \text{Br}^- > \text{SCN}^-$, and that of π -interaction is $\text{Br}^- > \text{SCN}^- > \text{Cl}^-$.

Key words: Spectroelectrochemistry, Dirhodium(II) Complexes, Cyclic Voltammetry

Introduction

Acetate bridged dirhodium(II), with lantern structure, is one of the earliest examples of binuclear complexes containing a metal-metal bond [1]. The surprisingly short Rh–Rh distance of 2.386(3) Å found in $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ compared to 2.69 Å in rhodium metal, was interpreted to imply multiple metal-metal bonds [2] rather than a single bond, which would be predicted for a d^7 – d^7 system using a MO approach [3]. Today it is generally agreed that the rhodium-rhodium bond order is unity in binuclear rhodium(II) complexes [4].

In the last three decades a large number of carboxylate bridged dirhodium(II) complexes, with or without axial ligands, have been prepared and their molecular structures determined [5]. A great deal of effort was spent to understand the effect of the nature of bridging and axial ligands on the molecular structure, the metal-metal distance, the electronic structure, and the electrochemical properties of the complexes. The interest in carboxylate bridged dirhodium(II) complexes, $[\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2]$, has also originated from their

potential practical applications as anti-tumor agents [6], catalysts in organic synthesis [7], stationary phases for gas chromatography [8], and liquid crystals (with long R-groups) [9].

The electronic absorption spectrum of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ in water contains four bands in the range of 600 to 200 nm. The two lower energy bands are weak ($\epsilon = 215$ and $106 \text{ cm}^{-1} \text{ M}^{-1}$), and the two higher energy bands are intense ($\epsilon = 4000$ and $17000 \text{ cm}^{-1} \text{ M}^{-1}$). The assignment of the spectra and the energy order of the frontier molecular orbitals have been the subject of many experimental [10] and theoretical studies [4, 11]. Unfortunately, generally accepted assignments of the absorption bands and the energy order of the molecular orbitals are still lacking. One of the major problems is related to the assignment of the two lower energy bands in the absorption spectra of $[\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2]$ complexes. These bands were assigned to fully allowed dipole transitions in almost all the works reported. Even though this problem has been mentioned [12], no convincing argument has appeared so far in the literature explaining why these fully allowed transitions have such low molar absorptivities.

Studies by Sowa *et al.* [13] on the electronic absorption spectra of neutral complexes of the type $[\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2]$ ($\text{R} = \text{Et}, \text{CF}_3$; $\text{L} = \text{H}_2\text{O}, \text{N}(\text{H}_4\text{C}_2)_3\text{CH}, \text{PPh}_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3$), and their cation radicals showed that the “metal-axial ligand” interactions are stronger than the “metal-metal” interactions, and that π -back bonding between rhodium and the axial ligand is very weak. On the other hand, Drago *et al.* [14] based on their ESR and base adducts studies, suggested that the π -bonding between rhodium and the axial ligand is important.

Dirhodium(II) complexes bridged with carbonate [15], sulphate [15, 6], and dihydrogenphosphate [17] ligands were also prepared and their crystal structures have been determined. All three complexes have the same lantern structure as $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ with short Rh–Rh distances (2.378(1) Å for carbonate [18]; 2.450(2) Å for sulphate [19]; 2.487(1) Å for dihydrogenphosphate [20]). The electronic absorption spectra are very similar [15, 21]. Studies on these complexes are very limited compared to carboxylate bridged dirhodium(II) analogues.

In this work we prepared the title complexes and studied their electrochemical and spectroelectrochemical behaviour, in order to further our understanding of the electronic structure, the metal-axial ligand interactions, and the effect of bridging and axial ligands on the oxidation and reduction potentials.

Experimental Section

Preparation and identification of compounds

$\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2$: This complex was prepared by a well-established literature procedure [22]. $\text{Rh}_2\text{C}_{10}\text{H}_{20}\text{O}_{10}$ (506.1): calcd. C 21.74, H 2.74; found C 21.54, H 2.70. UV/vis (CH_3CN): λ_{max} ($\lg \epsilon$) = 552 nm (2.41), 438 nm (2.18), 333^{sh} nm (2.24), 246^{sh} nm (3.78), 220 nm (4.28); UV/vis (H_2O): λ_{max} ($\lg \epsilon$) = 586 nm (2.33), 440 nm (2.03), 250^{sh} nm (3.60), 218 nm (4.23).

$\text{Na}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]$: This compound was prepared by using the following modified literature method [15]. 0.248 g (0.49 mmol) of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ and 5 ml of a 2 M Na_2CO_3 solution were placed in a 20 ml round bottom flask connected to a reflux condenser. The flask was immersed in an oil bath at 60 °C while stirring. The temperature of the oil bath was slowly increased to 120 °C. The temperature was

then allowed to drop to 100 °C and the mixture was kept at 100 °C for about 1 h. The colour of the solution changed to blue. The solution was first cooled to room temperature, and then in an ice bath. The blue solid was collected by filtration and dissolved in about 40 ml of water. To the dark blue solution about 40 ml of methanol was added and a blue precipitate formed. The solution was cooled and the precipitate was collected by suction filtration using sintered glass, washed with small amounts of cold water, methanol and ether. (Yield: 60%). $\text{Na}_4\text{Rh}_2\text{C}_4\text{O}_{14}\text{H}_4$ (573.8): calcd. C 8.37, H 0.70; found C 8.86, H 0.88. UV/vis (H_2O): λ_{max} ($\lg \epsilon$) = 594 nm (2.37), 398 nm (2.29), 266^{sh} nm (3.18), 226^{sh} nm (4.21), 200 nm (4.41).

$[\text{NH}_4]_4[\text{Rh}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$: This compound was prepared by using the following modified literature method [16(b)]. 0.402 g (0.80 mmol) of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ was dissolved in 10 ml of concentrated H_2SO_4 and this mixture was heated under nitrogen in a silicone oil bath to 130 °C for about 20 h. The colour of the solution changed from dark red to dark green. The solution was cooled in an ice bath, the green precipitate was collected and dried at room temperature. The green solid was dissolved using a minimum amount of water. The bluish-green precipitate formed upon dropwise addition of saturated $[\text{NH}_4]_2\text{SO}_4$ (aq) solution was collected and dried at room temperature (Yield: 34%). $\text{Rh}_2\text{S}_4\text{O}_{20}\text{N}_4\text{H}_{24}$ (734.3): calcd. H 3.29, N 7.62, S 17.47; found H 3.29, N 7.63, S 17.46. UV/vis (H_2O): λ_{max} ($\lg \epsilon$) = 628 nm (2.10), 424 nm (1.78), 298 nm (2.58), 242 nm (4.28), 200 nm (4.40).

$[\text{Rh}_2(\text{H}_2\text{PO}_4)_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$: This compound was prepared using the following slightly modified literature method [17]. 0.401 g (0.80 mmol) of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ and 5 ml of concentrated H_3PO_4 (85%) were placed in a 50 ml round bottom flask immersed in an oil bath at 44 °C and connected to a reflux condenser. The temperature of the solution was raised slowly to 150 °C with stirring and kept at that temperature for about 11 h. The solution was cooled to room temperature and maintained in the refrigerator overnight. Green solid particles formed and settled. The green mother liquor was decanted carefully and 5 ml of H_3PO_4 (85%) was added onto the remaining green precipitate. This fresh solution was refluxed again at around 150 °C for 11 h. After this process, the solution was cooled to room temperature and then kept in the refrigerator for 2 h. All green particles settled and the green mother liquor was separated very carefully and the remaining green solid was dissolved in a minimum amount

of water. The green aqueous solution was filtered in order to remove undissolved particles. The clear aqueous filtrate was evaporated in an oil bath at 110 °C–150 °C till green crystals were observed. The solution was cooled in an ice bath and green crystals were collected by filtration, washed with ice-cold alcohol and dried in a vacuum (Yield: 34%). $\text{Rh}_2\text{P}_4\text{O}_{19}\text{H}_{14}$ (647.8): calcd. C 0.00, H 2.18; found C 0.38, H 2.32. UV/vis (H_2O): λ_{max} (lg ϵ) = 666 nm (2.03), 466 nm (1.75), 402 nm (1.89), 286^{sh} nm (2.65), 242 nm (4.30).

Electrochemistry

Cyclic voltammetry measurements were performed using the Potentiostan Wenking POS 73 Potentiostat with a Lloyd PL3 XY/t recorder. In this system, Ag/AgBF₄ (0.1 M in CH₃CN) or SCE (saturated calomel electrode) were used as the reference electrodes. Platinum bead and platinum wire electrodes were employed as the working and the auxiliary (counter) electrodes, respectively. CV measurements were recorded in acetonitrile–tetrabutylammonium tetrafluoroborate, TBABF, water–Na₂SO₄ solvent–electrolyte couples at room temperature. Nitrogen or argon gas was allowed to pass through the solution before taking voltammograms to eliminate oxygen from the system. The concentration of the complexes was about 0.001 M for each measurement, and the voltage scan rate during the recording of CV was 100 mV/s.

Controlled potential electrolysis at the oxidation peak potential was carried out in UV-grade acetonitrile using TBABF as a supporting electrolyte. The changes in the electronic absorption spectra were recorded *in situ* [23], using an HP 8453A Diode Array Spectrophotometer during the electrolysis. Two platinum gauze electrodes were used as the working and the counter electrodes. An Ag-wire electrode was the reference electrode after making the correction between the Ag-wire and other reference electrodes, Ag/Ag⁺ and SCE (about 0.5 V for Ag/Ag⁺ and 0.4 V for SCE). Argon gas was bubbled through the electrolysis solutions for stirring purposes.

Results and Discussion

Molecular orbitals

Before we discuss our electrochemical oxidation and reduction results, which involve removing an electron from the HOMO and adding an electron to the LUMO, it is appropriate to consider the possible frontier molecular orbitals in bridged di-

rhodium(II) complexes. A qualitative molecular orbital energy level diagram for $[\text{Rh}_2(\text{B-B})_4\text{L}_2]$ (B-B = bridging ligand, L = axial ligand), with D_{4h} symmetry, is given in Fig. 1. The metal-metal bonding interaction in a $[\text{Rh}_2(\text{B-B})_4]$ complex results from the overlap of four d-orbitals, d_z^2 , d_{xy} , d_{xz} and d_{yz} [3]. The axial ligand σ - and π -symmetry orbitals interact with these Rh–Rh moiety molecular orbitals. The examination of the diagram shows that σ -interactions of axial ligands will increase the energies of $\sigma_{(\text{Rh}-\text{Rh})}$ and $\sigma^*_{(\text{Rh}-\text{Rh})}$, π -donor interactions will increase the energies of $\pi_{(\text{Rh}-\text{Rh})}$ and $\pi^*_{(\text{Rh}-\text{Rh})}$, and π -acceptor interactions will decrease the energies of $\pi_{(\text{Rh}-\text{Rh})}$ and $\pi^*_{(\text{Rh}-\text{Rh})}$ orbitals, going from $[\text{Rh}_2(\text{B-B})_4]$ to $[\text{Rh}_2(\text{B-B})_4\text{L}_2]$. The energies of $\delta_{(\text{Rh}-\text{Rh})}$ and $\delta^*_{(\text{Rh}-\text{Rh})}$ are not expected to change significantly upon axial ligand bonding. Thus the relative energy order of the Rh–Rh moiety molecular orbitals will be determined by the nature of the Rh-axial ligand interactions in $[\text{Rh}_2(\text{B-B})_4\text{L}_2]$.

$$[Rh_2(O_2CCH_3)_4(CH_3OH)_2]$$

The CV which was taken in acetonitrile at room temperature vs an Ag/Ag^+ reference electrode

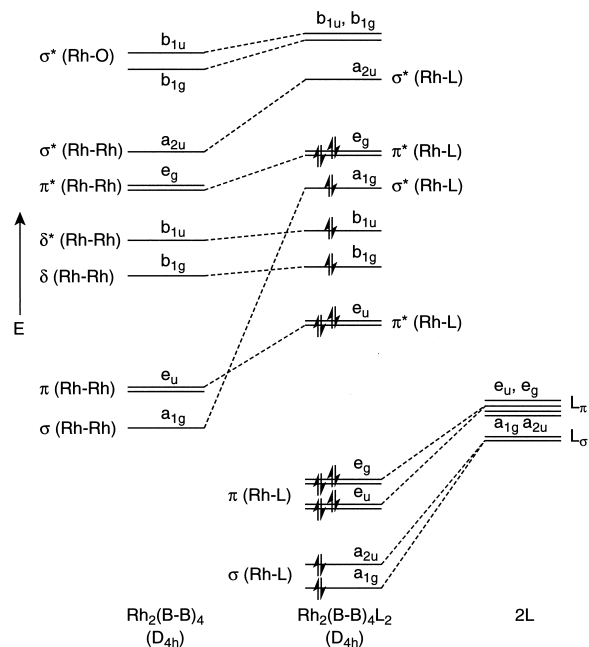


Fig. 1. The molecular orbital energy level diagram for $[\text{Rh}_2(\text{B-B})_4\text{L}_2]^n$, emphasizing Rh-axial ligand interactions.

contains a reversible oxidation peak at +0.80 V at the first anodic scan. Upon reversal of the scan direction, no additional cathodic peak was observed. This oxidation corresponds to the removal of one electron from the rhodium centers, yielding a Rh(II)–Rh(III) cation complex, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$ [10(b), 13, 24], which is expected to be paramagnetic.



The acetonitrile solution of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ was electrolysed at the oxidation peak potential (+1.30 V) in its CV, *versus* Ag-wire reference electrode. The changes in the absorption spectrum of the complex were followed *in situ* by measuring the spectra during the electrolysis at 200 mC intervals (Fig. 2(a)). The electronic absorption spectrum of the neutral complex in acetonitrile contains two bands at 438 and 552 nm in our working range of 300–950 nm. During the oxi-

dative electrolysis these bands disappeared, while new bands at 798 and 506 nm formed. The isosbestic points at 614 and 536 nm remained sharp until one electron per dimer was transferred. These observations are consistent with the electrolysis reaction giving in eq. (1). Thus the final spectrum of the electrolysis solution must be the absorption spectrum of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2^+$.

Cyclic voltammetry data reveal that the oxidation of a Rh(II)–Rh(II) complex to a Rh(II)–Rh(III) complex is reversible. If this is so, then the Rh(II)–Rh(III) mixed valent complex cation should also be reduced back to the original complex by reductive electrolysis. In order to check this, an electrochemically oxidized solution of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2$, which presumably contained only $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$, was electrochemically reduced at constant potential corresponding to the reduction peak potential in the CV. The changes in the electronic absorption spectrum during the reductive electrolysis were recorded *in situ* (Fig. 2(b)). The spectral changes indicate complete reversibility.

The oxidized solution (Fig. 2(a)) was too concentrated to get spectroscopic data below 300 nm. In order to obtain the spectral features of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2^+$ between 300–200 nm, the electrochemically oxidized acetonitrile solution was diluted stepwise, and the spectrum of each solution measured. The spectra obey Beer's Law as shown in Fig. 3 and as tabulated in Table 2. There are more features in the spectrum compared to that of Rh(II)–Rh(II) complex. Band V at 324 nm is very broad and probably originates from two different transitions.

Electrochemical and chemical oxidation of acetate bridged dirhodium(II) complexes have been

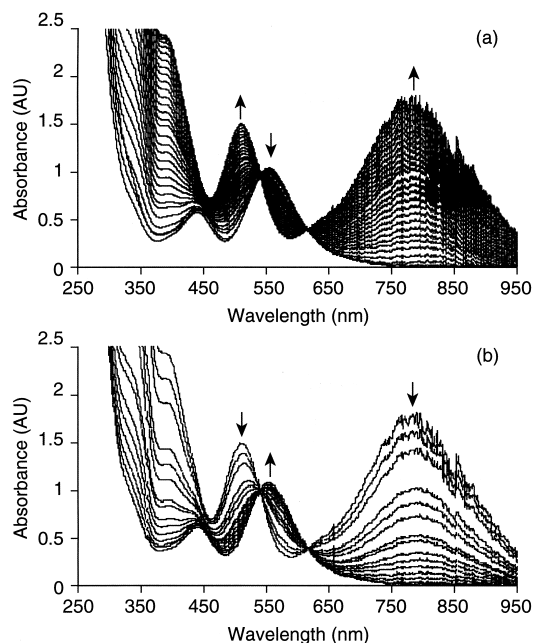


Fig. 2. The changes in the electronic absorption spectrum of 4.3×10^{-3} M $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ during the electrochemical, (a) oxidation at 1.30 V (b) followed by reduction at 0.00 V, vs Ag wire in acetonitrile. There are 200 mC intervals between two scans.

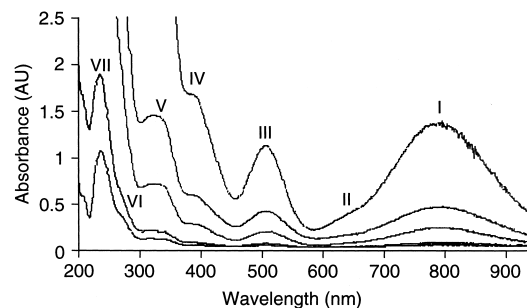


Fig. 3. The electronic absorption spectrum of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$ in acetonitrile.

reported in the literature [10(b), 24], but the quantitative UV-vis spectrum of the Rh(II)–Rh(III) species accurately measured in this work for the first time. It has been suggested that the radical complex is not very stable in solution, but decomposes back to the original Rh(II)–Rh(II) dimer and monomeric Rh(III) complexes [10(b)]. The mechanism of the decomposition reaction is not known. Our results show that the decomposition below 20 °C is negligible for a period of a few hours. The decomposition reaction rate is very much temperature dependent and increases with increasing temperature. At present, we are investigating the temperature dependence and the mechanism of this decomposition reaction. Our preliminary results rule out disproportionation.

The spectrum of the $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]$ complex is about 5000 cm^{-1} red-shifted when it is oxidized to $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$. This effect is particularly clear for the two lowest energy bands. The red shift going from the “ Rh_2^{4+} ” to the “ Rh_2^{5+} ” system is consistent with the transitions being LMCT type excitations. Therefore, the weak lower energy bands may be assigned to the dipole forbidden transitions from the bridging oxygen lone pairs to the $\sigma^*_{(\text{Rh}-\text{Rh})}(2a_{2u})$ orbital ($^1A_{1g} \rightarrow ^1E_g, ^1A_{1g}, ^1B_{1g}$).

The rhodium-axial ligand donor atom distances are always longer than expected for single bond distances. For example, the Rh–O_{equatorial} distance is 2.04 Å, while the Rh–O_{axial} distance is 2.30 Å [2(a)]. The weakness of the Rh-axial bonds manifests itself in fast axial ligand replacement reactions [25]. When $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$ or $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ are dissolved in a donor solvent, such as acetonitrile or water, the axial positions are occupied by solvent molecules. If any potential ligand species is present in solution it readily replaces the solvent molecules at the axial position. In this work, we have prepared solution species of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2]^{2-}$, where $\text{L} = \text{Cl}^-, \text{Br}^-, \text{SCN}^-$ by addition of excess ligand L to the solution of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]$ in water. The replacement of the axial solvent molecules by the ligands L is witnessed by the appearance of a characteristic band in the absorption spectrum [26]. This band is assigned to $\sigma_{\text{Rh}-\text{L}}(a_{1g}) \rightarrow \sigma^*_{\text{Rh}-\text{L}}(a_{2u})$ transition [10(g)]. Our CV and spectroscopic data for these complexes are collected in Table 1.

Inspection of the data in Table 1 reveals that the first oxidation potential in the CV of all the complexes is reversible and very much axial ligand dependent. The position of the characteristic absorp-

L	<i>n</i>	Solvent/ electrolyte	E _a , Volt ^a	Reference electrode	λ_{max} , nm (ϵ_{max} , M ⁻¹ cm ⁻¹)
B-B = CH ₃ CO ₂ ⁻					
CH ₃ CN	0	CH ₃ CN/Bu ₄ NBF ₄	0.80	Ag/Ag ⁺	
CH ₃ CN	0	CH ₃ CN/Bu ₄ NBF ₄	1.30	Ag Wire	
H ₂ O	0	H ₂ O/Na ₂ SO ₄	1.05	SCE	
Cl ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.15	SCE	270 (11270)
Br ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.60	SCE	290 (18270)
SCN ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.35	SCE	318 (16125)
B-B = CO ₃ ²⁻					
H ₂ O	-4	H ₂ O/Na ₂ SO ₄	0.35	SCE	
Cl ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.35	SCE	250 (18400)
Br ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.45	SCE	270 (30840)
SCN ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.30	SCE	296 (34630)
B-B = SO ₄ ²⁻					
H ₂ O	-4	H ₂ O/Na ₂ SO ₄	0.95	SCE	
Cl ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.25	SCE	272 (21790)
Br ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.45	SCE	298 (31790)
SCN ⁻	-6	H ₂ O/Na ₂ SO ₄	-0.30	SCE	326 (26380)
B-B = H ₂ PO ₄ ⁻					
H ₂ O	0	H ₂ O/Na ₂ SO ₄	0.55	SCE	
Cl ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.40	SCE	270 (25070)
Br ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.60	SCE	292 (25055)
SCN ⁻	-2	H ₂ O/Na ₂ SO ₄	-0.40	SCE	320 (27900)

Table 1. Cyclic voltammetry (VSR = 100 mV/s), and the electronic absorption (for the characteristic band) spectral data for $[\text{Rh}_2(\text{B-B})_4\text{L}_2]^n$ complexes.

^a Reversible oxidation peak potential.

Table 2. Electronic absorption spectral data for $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2]^+$ in acetonitrile.

Band No.	λ_{max} , nm	ν_{max} , μm^{-1}	ϵ_{max} , $\text{M}^{-1} \text{cm}^{-1}$
I	798	1.25	507
II	644(sh)	1.55	185
III	506	1.98	433
IV	385	2.60	642
V	324	3.09	1630
VI	268(sh)	3.73	5632
VII	237	4.22	16490

tion band is also shifted to lower energy on going from Cl^- to Br^- , or to SCN^- . The HOMO in these complexes is $\pi^*_{(\text{Rh-L})}(\text{e}_g)$ [11(c)]. Since this is an antibonding π -symmetry orbital between the Rh_2^{4+} and the axial ligands (Fig. 1), the energy of this orbital will increase as the π -donor character of the axial ligand increases. The higher the energy of this orbital the lower will be the oxidation potential. With this argument, the oxidation potential of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2]^n$ will reflect the degree of π -bonding between rhodium and the axial ligand. The oxidation potentials are 1.05, -0.15 , -0.35 , and -0.60 V for $\text{L} = \text{H}_2\text{O}$, Cl^- , SCN^- , and Br^- , respectively, suggesting that the π -donor order of these axial ligands is $\text{H}_2\text{O} < \text{Cl}^- < \text{SCN}^- < \text{Br}^-$. This order is also consistent with the π -donor order obtained from the spectrochemical series [27].

On the other hand, the energy of the characteristic band in the absorption spectrum will depend on the energy difference between the $\sigma_{(\text{Rh-L})}(\text{a}_{1g})$ and $\sigma^*_{(\text{Rh-L})}(\text{a}_{2u})$ molecular orbitals (Fig. 1). The stronger the σ -bonding interaction between the rhodium and the axial ligand, the higher will be the energy difference between these two orbitals. Thus the energy of the characteristic band will reflect the degree of Rh-L σ -interaction. Our data are consistent with the σ -donor power as $\text{Cl}^- > \text{Br}^- > \text{SCN}^-$.

$\text{Na}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]$, $(\text{NH}_4)_4[\text{Rh}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$, $[\text{Rh}_2(\text{H}_2\text{PO}_4)_4(\text{H}_2\text{O})_2]$

These complexes are not soluble in acetonitrile, therefore all electrochemical and spectral measurements were made in aqueous solutions. The electronic absorption spectra are very similar to that of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$, both in intensity and pattern-wise. This observation suggests that the electronic spectrum results from the same electronic excitations.

Cyclic voltammetry and some spectral data are included in Table 1. Each CV contains a reversible oxidation peak. The number of electrons transferred during the electrochemical oxidation at the peak potential was found to be one-electron/dimer using a digital coulometer. The electron is removed mainly from the metal based orbital as in the case of the acetate bridged complex. The oxidation potential of the carbonate complex (0.35 V) is significantly lower than for acetate (1.05 V), sulfate (0.95 V) or dihydrogenphosphate (0.55 V) complexes. This may be due to the higher electron donating power of the carbonate and also stronger metal-metal interactions. Both effects will increase the energy of the HOMO, $\pi^*_{(\text{Rh-L})}(\text{e}_g)$. In fact the Rh-Rh distance is the shortest (2.378(1) Å) in the carbonate complex compared to the others.

In order to see the effect of the axial ligands on the oxidation potential, $[\text{Rh}_2(\text{CO}_3)_4\text{L}_2]^{6-}$, $[\text{Rh}_2(\text{SO}_4)_4\text{L}_2]^{6-}$, and $[\text{Rh}_2(\text{H}_2\text{PO}_4)_4\text{L}_2]^{2-}$ ($\text{L} = \text{Cl}^-$, Br^- , SCN^-) were prepared in solution by adding an excess amount of L , and the CV's were measured. Reversible oxidation peak potentials along with characteristic absorption band data are presented in Table 1. Careful examination of the data in Table 1 shows a remarkable similarity in the trend of oxidation potential changes and the relative positions of the characteristic bands to that of the acetate bridged dirhodium(II) complex. In all cases the oxidation becomes much easier when the axial water ligands are replaced by chlorides, bromides, or thiocyanates. Going from dichloro to dibromo, the oxidation potential is lowered by 0.45, 0.15, 0.20 and 0.20 V for acetate, carbonate, sulphate and dihydrogenphosphate complexes, respectively. This result suggests that the acetate-bridged dirhodium(II) complex is more discriminating towards the π -interaction of the axial ligand compared to the others. On the other hand, the changes in the position of the characteristic band from one type of the axial ligand to the other are very close to each other and to the changes observed for the acetate complex. This result suggest that the relative order of σ -bonding of the axial ligands with the rhodium atoms in all these complexes is the same. With the same argument used for acetato-bridged dirhodium(II) complexes, the data given in Table 1 indicate that the σ -bonding order is $\text{Cl}^- > \text{Br}^- > \text{SCN}^-$ and the π -bonding order is $\text{Br}^- > \text{SCN}^- \cong \text{Cl}^-$.

Conclusion

The first oxidation peak in the CV of all complexes studied in this work is reversible and corresponds to a one electron transfer from a metal-based orbital. The electrochemical oxidation of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^0$, (Rh(II)–Rh(II)), yields the mixed valent cation complex $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$ (Rh(II)–Rh(III)). This cation is very stable in acetonitrile solution below 20 °C and can be electrochemically reduced back to the original Rh(II)–Rh(II) complex. The UV-vis electronic absorption spectrum of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^+$ is redshifted with respect to the spectrum of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2]^0$.

When the axial ligands are Cl^- , Br^- and SCN^- , the first oxidation peak potentials have a relative order $\text{Cl}^- \geq \text{SCN}^- > \text{Br}^-$ for all complexes studied in this work. Since the electron is removed from a

$\pi^*_{(\text{Rh}-\text{Rh})}$ molecular orbital in all cases, the oxidation potential will reflect the energy of this orbital. The energy of this orbital is determined by the degree of π -donor interaction of the axial ligands, making the Br^- ligand the strongest π -donor, and the Cl^- ligand the weakest in these complexes.

A characteristic band appears in the spectra of the complexes when the axial water ligands are replaced by Cl^- , Br^- and SCN^- . This band results from a $\sigma_{(\text{Rh}-\text{L})} \rightarrow \sigma^*_{(\text{Rh}-\text{L})}$ excitation and its energy is determined by the degree of σ -donation of the axial ligand. In our case, the energy order of the characteristic band is $\text{Cl}^- > \text{Br}^- > \text{SCN}^-$. This observation suggests that, as an axial ligand, Cl^- is the strongest σ -donor and SCN^- is the weakest.

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