Electrochemical and Spectroelectrochemical Studies on Three Dinuclear Rhodium(II) Complexes with O-Oxypyridine Anions as Ligands

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Abstract

The electrochemical oxidation of $Rh_2(hp)_4$, $Rh_2(chp)_4$ and $Rh_2(mhp)_4$ has been examined by cyclic, alternating current and stirred voltammetry in nine non-aqueous solvents. The oxidation potentials depend upon the identity of the solvent, and become more cathodic as the donor power of the solvent is increased. In any given solvent an apparent correlation exists between the three oxidation potentials and the Taft resonance parameter for the variously substituted pyridyl rings. The stable one-electron oxidation products have been characterised spectroelectrochemically in CH_3CN. The electro-generated monocations exhibit characteristic inter-valence charge-transfer bands in the near infrared portion of their electronic spectra.

Introduction

For many years the synthesis and X-ray structural characterisation of dinuclear rhodium(II) compounds have received much attention in the literature [1–3]. In more recent times however the emphasis in this area has shifted, at least in part, to investigations into the redox properties of these compounds. One reason for this shift is that electron-transfer reactions can play a crucial role in the catalytic [4–6] and biological [7–11] activities of these molecules. For example, while it has been shown that Rh_2-$(O_2CR)_4$ compounds are potent inhibitors of Ehrlich ascites, L1210 ascites and P388 tumours in mice, it has also been demonstrated that the singly oxidised complex $[Rh_2(O_2CR)_4]^+$ displays greater antitumour activity.

The redox properties of the tetracarboxylate complexes have been extensively studied [12–18]. Wilson and Taube studied the aqueous oxidation of $Rh_2(O_2CCH_3)_4$ with ceric ion potentiometrically [12, 13]. They observed that the dirhodium complex could be reversibly oxidised in a single electron transfer. The potential of the oxidation was dependent on the pH of the medium. Bear *et al.* examined the electro-oxidation, electro-reduction reactions of ten $Rh_2(O_2CR)_4$ compounds in a number of solvents [16]. They observed that the mid-point potentials depended upon the identity of both the carboxylate and the solvent. The potential for the $[Rh_2]^{4+/5+}$ couple was sensitive to the electron-donating, electron-withdrawing power of the substituent group, R, of the carboxylate and an approximately linear relationship was observed between that potential and the Taft inductive parameters for the variously substituted carboxylates. For a given carboxylate complex it was found that the oxidation potential was inversely related to the solvent's donor ability, plots of $E°$ *versus* Gutmann's Donor Number being approximately linear. Drago *et al.* [17] investigated the electro-oxidation of a group of 1:1 and 1:2 adducts of $Rh_2(O_2CC_3H_7)_4$ in dichloromethane. They observed that the 1:2 adducts were more easily oxidised than the 1:1 adducts. More recently similar observations have been made by Bottomley and Hallberg [18].

Recently much attention has been devoted to the tetra-amidate complexes $Rh_2(RNC(O)R')_4$ [19–22]. It has been observed that changing the coordination sphere about the $[Rh_2]^{4+}$ core from one of eight oxygen atoms to one comprising four oxygen and four nitrogen atoms shifts the oxidation potentials to values which are 700–1000 mV more cathodic. For example the parent acetate complex $Rh_2(O_2CCH_3)_4$ undergoes a quasireversible one-electron oxidation in acetonitrile at +1.17 V *versus* S.C.E., whereas the corresponding oxidation occurs at +0.15 V for the compound $Rh_2(HNC(O)CH_3)_4$ under similar experimental conditions [21]. Similar observations have been made for other pairs of dirhodium(II) compounds. In several cases this cathodic shifting of potentials is sufficiently dramatic for a second oxidation wave to be observed within the available solvent range [21, 22]. Unfortunately these new one-electron oxidation waves occur at potentials >1.40 V *versus* S.C.E., too close to the solvent background for any further characterisation of the doubly oxidised products to be feasible.

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When the remaining four oxygen atoms around the $[Rh_2]^{4+}$ core are replaced by nitrogen atoms, as is the case in the compounds $Rh_2\{Ph(2\text{-}pyr)N\}_4$ [23, 24] and $Rh_2(N_2Ph_2CPh)_4$ [25] the second oxidation wave occurs at less extreme potential. In the case of $Rh_2\{Ph(2\text{-}pyr)N\}_4$ that second oxidation wave occurs at +0.72 V *versus* Ag/AgCl, and the dication $[Rh_2\{Ph(2\text{-}pyr)N\}_4]^{2+}$ has been generated electrochemically and characterised by electronic spectroscopy. The compound $Rh_2(N_2Ph_2CPh)_4$ undergoes two reversible one-electron oxidation reactions analogous to those of $Rh_2\{Ph(2\text{-}pyr)N\}_4$; however, even more remarkably, it also undergoes a reversible one-electron reduction corresponding to the formation of a new dinuclear rhodium(II/I) species [25]. Although similar processes have been reported for positively charged $[L_{4-n}Rh_2(O_2\text{-}CCH_3)_n]^{(4-n)+}$ cations [26–28] these reduction reactions have been assigned as being ligand based, on ESR spectroscopic evidence. The ions $[Rh_2(N_2Ph_2CPh)_4]^{+/-}$ were generated electrochemically and characterised by ESR spectroscopy. The ESR spectrum of $[Rh_2(N_2Ph_2CPh)_4]^+$ is unique among those of dirhodium(II/III) complexes in that it showed non-equivalent rhodium centres.

In order to gain further insight into the influence of bridging and axial ligands upon the fascinating redox behaviour of this class of compound we decided to focus our attention upon compounds with O-oxypyridine anions as ligands. These ligands have some features in common with the amidate ions, namely coordination to rhodium through one oxygen and one nitrogen atom, as well as similarities with the ligand $[Ph(2\text{-}pyr)N]^-$: the inclusion of a pyridyl nitrogen atom in the bridging unit. In this paper we report the results of our extensive electrochemical and spectroelectrochemical investigations into the three compounds $Rh_2(hp)_4$, $Rh_2(chp)_4$ and $Rh_2(mhp)_4$, the bridging ligands of which are identified below, and compare these new results with those of earlier studies on related dirhodium(II) molecules.
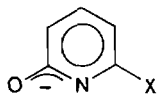
H = H, hp
X = Cl, chp
X = Me, mhp

Experimental

Preparations

The compounds $Rh_2(chp)_4$ and $Rh_2(mhp)_4$ were prepared from $Rh_2(O_2CCH_3)_4$ and either 6-chloro-2-pyridinol or 2-hydroxy-6-methylpyridine respec-

tively, using previously reported procedures [29]. The compound $Rh_2(hp)_4$ was prepared from $Rh_2(O_2CCH_3)_4$ and 2-hydroxypyridine by heating in a N_2 atmosphere to 150 °C for 72 h. On melting, the mixture rapidly turned pink, and if the reaction was stopped at this stage the adduct $Rh_2(O_2CCH_3)_4 \cdot 2Hhp$ could be isolated, but prolonged heating gave purple $Rh_2(hp)_4$. The excess ligand was removed by vacuum sublimation at 95 °C. Yield *ca.* 90%. *Anal.* Found: C, 41.6; H, 3.1; N, 10.0. Calc. for C_{20}-$H_{16}N_4O_4Rh_2$: C, 41.2; H, 2.8; N, 9.6%.

Instrumentation

Voltammetric studies employed a Metrohm E506 potentiostat interfaced with a Metrohm E505 cell-stand utilizing a 3-electrode geometry. The working electrode consisted of either a dropping mercury electrode (DME) or a platinum wire electrode (Metrohm EA285). A non-aqueous Ag, AgCl/Cl⁻, CH_2Cl_2 electrode was used as a reference electrode (Metrohm EA441/5) and a platinum wire as an auxiliary electrode. The reference electrode was separated from the bulk solution by a fritted salt-bridge. Cyclic voltammetric measurements also employed a Metrohm E612 VA Scanner in conjunction with a Hewlett Packard 7035B X-Y recorder. Measurements were made in a range of solvents (see Table I) containing 0.1 mol dm⁻³ of $[NBu^n_4][BF_4]$ as inert supporting electrolyte. De-aeration of the solution was performed before commencing each experiment and a stream of nitrogen was passed throughout. All potentials are reported with respect to the Ag/AgCl reference electrode (against which ferrocene is oxidised at +0.60 V).

The oxidation products $[Rh_2(hp)_4]^+$, $[Rh_2(chp)_4]^+$ and $[Rh_2(mhp)_4]^+$ were characterised by *in situ* electronic absorption spectroscopy, using a Varian 2300 UV/Vis/near infrared spectrophotometer and a Metrohm E506 potentiostat. An optically transparent thin layer electrode (OTTLE) cell was employed to generate the oxidised species in the beam path of the spectrophotometer, using a platinum gauze as the working electrode (*ca.* 60% transmitting), a non-aqueous Ag/Ag⁺, CH_3CN reference electrode, against which ferrocene was oxidised at a potential of +0.20 V, and a platinum wire auxiliary electrode. All three compounds were examined in CH_3CN solution, which had previously undergone rigorous purification, containing 0.1 mol dm⁻³ of $[NBu^n_4][BF_4]$ over the range 1500–200 nm.

Results and Discussion

Electrochemistry

The redox behaviour of the three complexes was examined in detail. Cyclic voltammetric measure-

TABLE I. Electrode Potentials and Electrochemical Parameters for the Oxidation of $Rh_2(hp)_4$, $Rh_2(chp)_4$ and $Rh_2(mhp)_4$ in Non-aqueous Media

Solvent	DN (kcal mol^{-1})	π^* (cm^{-1})	Compound		
			$Rh_2(hp)_4$	$Rh_2(chp)_4$	$Rh_2(mhp)_4$
dmso	29.8	1.000	+0.78	+1.44	
propylene carbonate			+0.75	+1.44	+1.21
acetonitrile	19.3	0.76	+0.82	+1.43	+1.16
acetone	17.0	0.68	+0.72	+1.42	+1.15
nitromethane	2.7	0.80	+0.88	+1.39	+1.14
benzonitrile			+0.76	+1.40	+1.10
ethanol	21.0	0.85	+0.72	+1.20	+1.00
dmf	26.6	0.875	+0.66	+1.21	+0.99
pyridine	33.1	0.867	+0.63	+1.20	+0.92

ments show that each compound undergoes a single oxidation process in the potential range +0.625 to +1.44 volts. Experiments were performed at scan rates from 20 to 2000 mV s^{-1}. Characteristic plots of i_p versus $\nu^{1/2}$ were linear and the ratio $i_{p\text{return}}/i_{p\text{forward}}$ was unity in each case. The potential separations, ΔE_p, varied between 55 and 120 mV depending on the solvent employed. These separations are closely similar to those found for the ferrocene/ferrocinium couple measured on our instrumentation under analogous conditions. Therefore the oxidation response for each compound shows typical characteristics of a reversible, diffusion controlled, one-electron charge-transfer process [30].

a.c. voltammetric measurements confirm the nature of the electron transfer reactions. Each voltammogram contains a single highly symmetrical peak, at a potential closely similar to the corresponding $E_{1/2}$ value obtained by cyclic voltammetry, with peak widths in the range 90–110 mV.

Stirred voltammograms exhibit well defined waves, with half-wave potentials close to those obtained from the C.V. and a.c.V. measurements. Plots of $\log(i/i_d - i)$ versus E give straight lines with gradients of approximately 60 mV. Confirmation of the one-electron nature of these processes was obtained by comparing the diffusion-limited currents with those obtained from known quantities of ferrocene. No further oxidations were observed up to the solvent limits.

The potential at which the $[Rh_2]^{4+}$ core undergoes oxidation is not only a function of the bridging ligand, but is also dependent on the solvent medium employed, as illustrated in Table I. To eliminate the effect of liquid junction potentials, all potentials were measured against that of the ferrocene/ferrocenium couple in the same solvent and the tabulated values quoted against an Ag/AgCl reference electrode at which ferrocene was oxidised at +0.60 volts. Potential intervals for each of the compounds are in the range 250–300 mV.
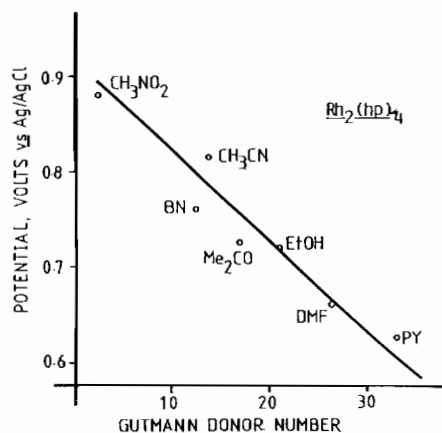

Fig. 1. Plot of reversible half-wave potential for the oxidation of $Rh_2(hp)_4$ vs. Gutmann Donor Numbers.

The potential at which the complexes $Rh_2(O_2-CR)_4$ are oxidised has been observed to vary linearly with the donor power of the solvent [16], as measured by the Gutmann Donor Number [31]. In general, as the donor ability of the solvent increased, and thus stronger axial bonds were formed with the complex, the oxidation potential was shifted to less positive potentials. This trend is also observed for other dirhodium(II) compounds, e.g. $Rh_2(O_2CCH_3)_2$-$(Ph_2P(C_6H_4))_2 \cdot 2L$ molecules [32].

When we plot the various oxidation potentials for $Rh_2(hp)_4$ against the appropriate Gutmann Donor Numbers then we clearly obtain a similar approximately linear correlation, Fig. 1. Analogous plots can be obtained from the data for the compounds $Rh_2(chp)_4$ and $Rh_2(mhp)_4$. The linearity of these plots indicates that the same mechanism for the oxidation reaction is operative in each of the solvents. The shift of potential with solvent donicity is an indication that the highest occupied molecular orbital, most probably the Rh–Rh π^* orbital, is destabilised with increased ligand binding ability.
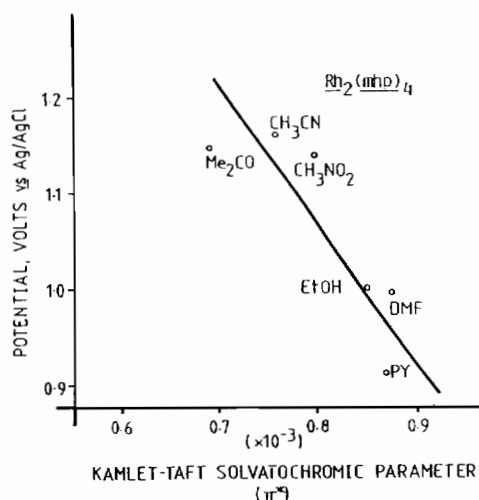
Fig. 2. Plot of reversible half-wave potential for the oxidation of $Rh_2(mhp)_4$ *vs.* π^*.

TABLE II. Electrode Potentials for the Oxidation of Rh_2-$(hp)_4$, $Rh_2(chp)_4$, and $Rh_2(mhp)_4$ in CH_3CN, with Corresponding Taft Inductive and Resonance Parameters

Compound	$E_{1/2}$	Substituent group	Inductive parameter (σ_I)	Resonance parameter (σ_R)
$Rh_2(hp)_4$	+0.82	H	0	0
$Rh_2(chp)_4$	+1.43	Cl	+0.47	−0.20
$Rh_2(mhp)_4$	+1.16	Me	−0.05	−0.10

It should be noted in passing that Gutmann Donor Numbers are only one of several possible empirical parameters which could be used to account for the main solvent effect upon redox potentials, albeit the most frequently employed [33]. Alternative parameters may be equally applicable and to amplify this point we have plotted the oxidation potentials for $Rh_2(mhp)_4$ against π^*, a Kamlet–Taft solvatochromic parameter [34], Fig. 2, and have obtained a second approximately linear correlation. Further examples could be provided. However, as each of these relationships is purely empirical it is unlikely that pursuit of this avenue will lead to a significantly more detailed understanding of solvent/compound/potential interrelationship.

We turn now to the influence of substituent groups in the bridging ligands on the redox potentials. The substituent groups are located at the 6-position of the pyridyl rings and irrespective of the solvent employed we observed a similar pattern in oxidation potentials for the three molecules. In every solvent it is $Rh_2(hp)_4$ which is most readily oxidised, while $Rh_2(chp)_4$ is the most difficult compound to oxidise. If the results reported here paralleled those obtained for the rhodiumtetracarboxylates then the dominant effect of the substituent group on the oxidation potential would be inductive in nature, a linear relationship having been observed between the oxidation potentials of variously substituted Rh_2-$(O_2CR)_4$ compounds and the Taft inductive parameters, σ_I, for the substituent groups, R [16]. However, this does not appear to be the case in this instance as the magnitude of the Taft inductive parameters for the H, Me and Cl groups (Table II) imply that the order of increasing oxidation potential would be $Rh_2(mhp)_4 < Rh_2(hp)_4 < Rh_2(chp)_4$, while the experimentally observed order, in CH_3CN, is

$Rh_2(hp)_4 < Rh_2(mhp)_4 < Rh_2(chp)_4$ (Table II). This observation is repeated in each of the solvents in which measurements have been made. Such an observation is surprising, as previously Taft inductive parameter/electrode potential correlations have been proven to be sufficiently sensitive to have been used to predict redox potentials, which have subsequently been confirmed by experiment [35]. Hence we must conclude that in this case at least the influence of the substituent group is not primarily an inductive one. Indeed if we examine the Taft resonance parameters, σ_R, for the appropriate substituent groups (Table II) we observed a trend in these values which parallels that observed for the potentials of the electron-transfer reactions. Clearly the resonance contribution to the free energy relationship is substantial; however, as yet we have no clear idea as to the mechanism by which that effect operates and further insights into this unexpected observation must await the preparation of additional examples of this class of compound.

Spectroelectrochemistry

Electronic spectra have been obtained, in CH_3CN solution, in the region 200–1500 nm for each of the neutral molecules and their related one-electron oxidation products using an OTTLE cell. The principle bands observed for each are listed in Table III, and Fig. 3 illustrates the spectra of $Rh_2(mhp)_4$ and $[Rh_2(mhp)_4]^+$ in the region 300–1300 nm. Only in the case of $Rh_2(mhp)_4$ can a sufficient concentration of the compound be maintained for bands in the visible region of the spectrum to be observed. However, each of the neutral molecules contains a series of intense high-energy bonds in the region 320–200 nm. The steady-state spectra obtained upon oxidation are little changed in this region of the spectrum and, assuming that the electron removed upon oxidation originated in the Rh–Rh π^* or δ^* orbital, it seems reasonable to conclude that these high energy transitions are localised on the ligand framework, with little or no metal character. The visible spectrum of $Rh_2(mhp)_4$ exhibits bands at 815 and 590 cm^{-1} with extinction coefficients of 1650 and 120 M^{-1} cm^{-1} respectively. If the

TABLE III. Principal Bands Observed in the Electronic Spectra of the Neutral and Monooxidised Complexes[a]

Complex	Neutral		Monooxidised	
	ν_{max} (nm)	ϵ (M^{-1} cm^{-1})	ν_{max} (nm)	ϵ (M^{-1} cm^{-1})
$Rh_2(hp)_4$	290	11450	810	1000
	228	42000	290	11450
			228	40450
$Rh_2(chp)_4$	315	6970	1005	2150
	263	27460	265	sh[b]
	231	44860	235	sh
$Rh_2(mhp)_4$	815	1650	980	4790
	590	120	765	2040
	310	6040	400	sh
	255	18700	255	20600
	228	39010	228	34580

[a]Measured in a 0.1 cm OTTLE cell using a Pt gauze electrode (*ca.* 60% transmitting) and CH_3CN solvent. [b]sh = shoulder.
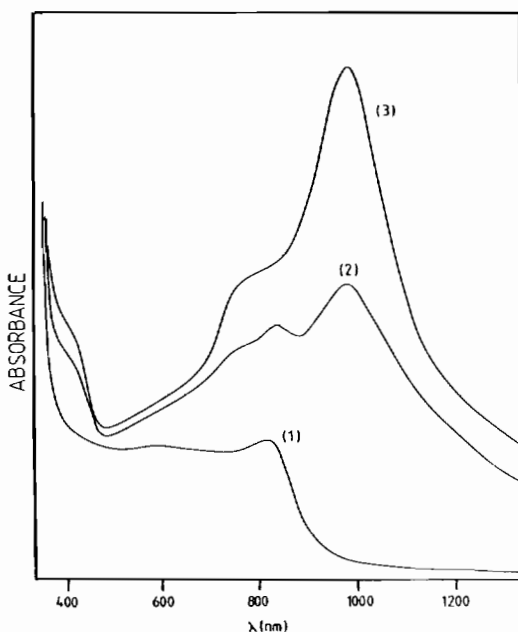

Fig. 3. Electronic absorption spectra obtained during the oxidation of 1×10^{-3} M $Rh_2(mhp)_4$ to yield $[Rh_2(mhp)_4]^+$ in CH_3CN, with 0.1 mol dm^{-3} of $[NBu^n_4][BF_4]$. $E_{applied}$ = +1.40 V. Total oxidation time per plot: (i) 0 s; (ii) 45 s; (iii) 300 s.

theoretical basis which has been developed for $[Rh_2(O_2CR)_4]^{0/+}$ molecules [36, 37] is valid in this system, and we have no guarantee of that fact, then we could tentatively assign the former transition to $0 \rightarrow \delta^*$ or $N \rightarrow \delta^*$ charge transfer, and the latter to a $\delta^* \rightarrow \sigma^*$ or $\pi^* \rightarrow \sigma^*$ transition. However, without further theoretical calculations such assignments remain purely speculative.

The removal of a single electron from a Rh–Rh antibonding orbital results in a formal increase in the Rh–Rh bond order, from unity to 1.5, and changes the formal oxidation state of the Rh_2 core from (II, II) to (II, III). Such changes in the electronic character of the metal core must result in considerable alterations in the metal–metal interaction. Upon oxidation the effect of such changes on the electronic spectra is most dramatic in the region 800–1100 nm (see Fig. 3). Concomitant with the oxidation of each compound is the development of a band in the near infrared portion of the electronic spectrum. The origin of these bands is as yet uncertain; however, we would like tentatively to suggest that they may be due to intervalence charge-transfer processes. Such processes have not usually been observed for Rh(II, III) compounds; however, this may be due to the fact that measurements have usually been restricted to the visible and UV portions of the spectrum. One recent report [38], on the rhodium(II, III) compounds $Rh_2(ap)_4X$ (ap = the anion derived from 2-aminopyridine; X = Cl or Br), does mention bands at about 1200 nm, although no attempt was made to assign these transitions. The presence of transitions above 800 nm may imply that the two rhodium ions are distinguishable. This observation is surprising, although not entirely unprecedented as Bear *et al.* have recently been able to observe non-equivalent rhodium centres in the cation $[Rh_2(N_2Ph_2CPh)_4]^+$ using ESR spectroscopy [25]. Also of note is the observation that the trend in inter-valence charge-transfer band position follows that of increasing ease of formation of the monocation, *i.e.* the complex which is easiest to oxidise, $Rh_2(hp)_4$, has the higest energy intervalence charge-transfer band in its monocation.

From both the present work using electronic spectroscopy and the work of Bear *et al.* using electrochemical ESR techniques [25] it would appear that the simple description of the one-electron oxidation products derived from dirhodium(II) tetrabridged compounds as completely delocalised is an oversimplification in particular instances. Further work on this phenomenon is in progress.

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