Inorganica Chimica Acta, 104 (1985) L15–L17

Synthesis and Spectroelectrochemical Characterisation of a Novel Rhodium(II) Dimer, $Rh_2(PhNpy)_4$

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Received May 16, 1985

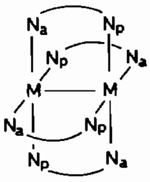
In recent years the electrochemical behaviour of binuclear rhodium(II) complexes has received considerable attention in the literature [1–12]. A common observation has been that the dinuclear unit, containing a $[Rh_2]^{4+}$ core, undergoes a single reversible one-electron oxidation to yield the related monocation. Extensive studies on the carboxylate complexes, $Rh_2(O_2CR)_4L_2$, have shown that the oxidation potential is influenced by the electronic effect of both the substituent group and the axial ligands [6, 7]. Recently several rhodium amidates $Rh_2(R'NC(O)R)_4$ have been investigated electrochemically [8–12]. On changing the immediate coordination sphere about the metal centre from one of eight oxygen atoms to one comprising four oxygen and four nitrogen atoms a shift in oxidation potentials to values which are 700–1000 mV less positive is observed. In the complexes $Rh_2(C_6H_5NC(O)CH_3)_4$ and $Rh_2(HNC(O)CH_3)_4$ this effect is sufficiently dramatic that a second oxidation wave, at potentials >1.40 V *vs.* S.C.E. [11, 12], can be observed in each case. Unfortunately the extreme potential and the close proximity of the solvent background precluded further studies on the doubly oxidised products.

We now report the synthesis of a new dirhodium(II) complex, one in which the immediate coordination sphere about the $[Rh_2]^{4+}$ core comprises eight nitrogen atoms. This new complex undergoes two facile one-electron oxidations at moderate potentials. The cations $[Rh_2(PhNpyr)_4]^{+/2+}$ have been characterised by *in situ* electronic absorption spectroscopy. The latter formally contains two Rh(III) centres and a double rhodium-to-rhodium bond.

Results and Discussion

The reaction of $RhCl_3 \cdot xH_2O$ with an excess of the sodium salt of 2-anilinopyridine (>10 fold) in refluxing ethanol gives a green solution. Extraction and subsequent recrystallisation yield a product with the empirical formula $[Rh(PhNpyr)_2]_n$**. The binuclear nature of the product has been confirmed by osmometry and by mass spectroscopy, where a parent ion peak at m/e = 882, corresponds to the binuclear cation $[Rh_2(PhNpyr)_4]^+$. The ^1H NMR spectrum shows only the presence of phenyl and pyridyl protons, as a series of multiplets between δ 6.70 and 8.30 ppm. The IR spectrum confirms that the ligands were present in their anionic form. The complex is essentially diamagnetic.

The complex does not readily form axial adducts suggesting that it has a symmetrical arrangement of bridging ligands, (**1**) or (**2**), where two pendant phenyl groups block each axial site, rather than the totally polar, type (**3**), arrangement.



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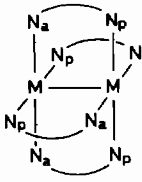

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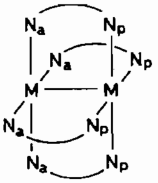

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(Na = amine nitrogen; N_p = pyridyl nitrogen)

A type (**1**) arrangement of ligands was observed in the Mo and W complexes, $M_2(PhNpyr)_4$ [13], while a type (**3**) arrangement has been observed in the Ru complex, $Ru_2(PhNpyr)_4Cl$ [14].

Cyclic (C.V.) and alternating current (a.c.V) voltametric measurements in CH_2Cl_2–0.5 M NBu_4BF_4, at a Pt electrode, at 294 K show that the complex undergoes two oxidation processes (Fig. 1). The first oxidation process, at $E_{1/2} = -0.01$ V, was diffusion controlled as shown by the characteristically constant plots of $ip/v^{1/2}$ and $E_{1/2}$ with increase in scan rate. In addition the difference in anodic and cathodic peak potentials, ΔEp, was equal to 65 ± 5 mV suggesting the abstraction of a single electron. The second oxidation, at $E_{1/2} = +0.64$ V, is chemically reversible although apparently characterised by sluggish heterogeneous charge-transfer kinetics [*i.e.* at 294 K, ip(anodic)/ip(cathodic) =

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**Satisfactory elemental analyses were obtained.

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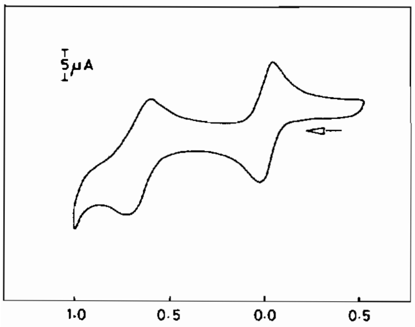

Fig. 1. Cyclic voltammogram of $Rh_2(PhNpyr)_4$ in CH_2Cl_2. Potentials *vs.* Ag/AgCl reference electrode (against which ferrocene is oxidised at +0.415 V).

1.0 at all scan rates (ν) from 50 to 500 mV s^{-1}, but ΔEp = 100 mV at ν = 50 mV s^{-1} and 140 mV at ν = 500 mV s^{-1}]. The one electron nature of both processes is indicated by the a.c.V. peak widths at half height (for both processes this was 100 mV at ω = 75 Hz) and confirmed by comparison of the diffusion limited currents with that of a known quantity of ferrocene, as measured by stirred voltametry. In addition an irreversible reduction wave was observed at a potential of Ep,c = −1.05 V, at 100 mV s^{-1}. Analogous reduction waves have been reported previously for other dirhodium(II) complexes but this process has never been fully investigated.

The controlled electrochemical oxidation of $Rh_2(PhNpyr)_4$ in an optically transparent cell has enabled us to determine the absorption spectra of the species $[Rh_2(PhNpyr)_4]^{0/+/2+}$ over a wide range.

Solutions of $Rh_2(PhNpyr)_4$ (1.33 mmol^{-1}) were oxidised at a platinum gauze optically active thin-layer electrode mounted in the spectrometer beam. Steady state spectra were recorded at potentials of −0.10, +0.20 and +0.75 V, in the range 1600–400 nm (Fig. 2).

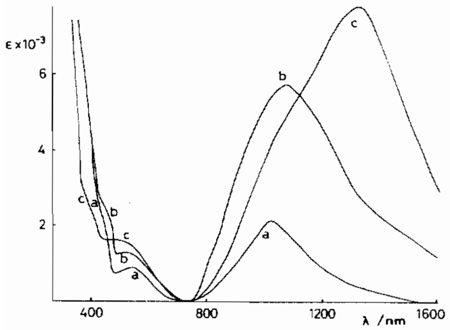

Fig. 2. Steady state electronic absorption spectra obtained at potentials of (a) −0.10 V, (b) +0.20 V, and (c) +0.75 V, in CH_2Cl_2–0.5 M NBu_4BF_4.

The neutral complex is characterised by a strong band in the near IR region, at 1015 nm, and a weaker band in the visible region, at 579 nm, a slight shoulder is also apparent at *ca.* 476 nm. The sequential oxidation of the complex is accompanied by the following changes in the spectrum.

The formation of the monocation, $[Rh_2(PhNpyr)_4]^+$, results in the growth and shifting to lower energy, 1066 nm, of the band in the near IR region. The peak in the visible region moves to higher energy, 525 nm, and increases in intensity. Oxidation at a potential *ca.* 100 mV more positive than the second wave results in further growth and shifting of the near IR band, to 1365 nm, together with continued increases in energy, to 500 nm, and extinction coefficient for the band in the visible region of the spectrum. These transitions are totally reversible since the spectra obtained after controlled potential reduction of the oxidised species were identical to those observed initially.

The ligand bridging system in this complex is considerably different from that of the tetra-carboxylates and any interpretation of the electronic spectra based upon extrapolation from the theoretical results [15–20] obtained on the simpler dirhodium systems would be speculative. However, it does not appear unlikely that the band in the visible region, initially at 579 nm and shifting to a final value of 500 nm, with a concomitant increase in extinction coefficient, could be assigned to a Rh–Rh $\pi^* \rightarrow$ Rh–Rh σ^* transition, while the magnitude of the extinction coefficient of the absorption in the near IR region suggests that it is due to a charge-transfer process. The smooth changes which occur in the spectra upon sequential oxidation suggest that the following description may be applied to the redox processes.

$$Rh_2(PhNpyr)_4 \underset{+e}{\overset{-e}{\rightleftharpoons}} [Rh_2(PhNpyr)_4]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} [Rh_2(PhNpyr)_4]^{2+}$$

That is, the metals are in the formal oxidation states +2, +2.5 and +3, and the respective metal-metal bonds are of the order 1.0, 1.5 and 2.0.

Clearly further experimental and theoretical studies are needed to unequivocally assign the electronic transitions in this system, and as the initial step towards this goal we are currently addressing the problem of the isolation and further characterisation of the oxidised products.

Acknowledgement

We thank Johnson Matthey plc for generous loans of rhodium trichloride.

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