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Preparation and some Properties of Two Binuclear Ruthenium Complexes, $Ru_2(RNpyr)_4Cl$, ($R = Me, PhCH_2$)

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Abstract

The compounds $Ru_2(MeNpyr)_4Cl$ (**1**) and $Ru_2(PhCH_2Npyr)_4Cl$ (**2**) have been prepared by the interaction of $Ru_2(O_2CCH_3)_4Cl$ with an excess of MeNHpyr (2-(methylamino)pyridine) and $PhCH_2NHpyr$ (2-benzylaminopyridine) at 90 and 120 °C, respectively. These air-stable compounds have been characterised by analytical and spectroscopic measurements. Electrochemical measurements show that the binuclear unit may be both oxidised and reduced while magnetic measurements indicate the presence of three unpaired electrons per $[Ru_2]^{5+}$ unit. Comparisons have been made with the recently reported related complex, $Ru_2(PhNpyr)_4Cl$ (**3**).

Introduction

For many years the multiple bond chemistry of ruthenium(II½) was largely restricted to that of the binuclear carboxylate complexes [1]. Recently however several amidates $Ru_2(R'NC(O)R)_4Cl$ [2–5] have been reported together with a number of more unusual complexes, namely $Ru_2(hp)_4ClHhp$ [6], $Ru_2(PhNpyr)_4Cl$ [6], and $Ru_2(chp)_4Cl$ [7], in which the four asymmetric ligands bridge the ruthenium-to-ruthenium bond in a 'totally polar' arrangement, such that the two metal centres are no longer equivalent.

The orbital pattern in these strongly metal–metal bonded complexes is sensitive to axial and equatorial ligand perturbations and Bear and Kadish have shown [2, 3] that the redox behaviour of the amidates, $Ru_2(R'NC(O)R)_4Cl$, is dependent upon the identity of the groups R and R', as well as upon the solvent in which the measurements are made. In the case of these amidates each ruthenium ion is coordinated by two oxygen and two nitrogen atoms [5]. Our interest is in those complexes in which each ruthenium is coordinated in the equatorial plane by four nitrogen atoms. The previously reported $Ru_2(PhNpyr)_4Cl$ is one example of such a complex [6]. The bridging ligand $[PhNpyr]^-$ (the anion derived from 2-anilinopyridine) is only one member of a family of ligands, RNHpyr. These ligands can be altered chemically by substitution on the amide nitrogen atom. In this paper we report the syntheses, physical properties, and electrochemical behaviour of two closely related diruthenium(II½) complexes, $Ru_2(RNpyr)_4Cl$ (R = Me, **1**; $PhCH_2$, **2**) and make comparisons with $Ru_2(PhNpyr)_4Cl$ (**3**).

Experimental

Materials

$Ru_2(O_2CCH_3)_4Cl$ was prepared by using a literature method [8]. All other reagents were purchased from normal commercial suppliers. 2-Benzylaminopyridine was purified by sublimation prior to use.

Synthesis

$Ru_2(PhCH_2Npyr)_4Cl$

A mixture of $Ru_2(O_2CCH_3)_4Cl$ (0.2 g, 0.4 mmol) and 2-benzylaminopyridine (5.0 g, 27 mmol) was placed in a Schlenk tube in an oil bath. The temperature was raised to 120 °C and the mixture stirred for 16 h. The initial orange–brown colouration was rapidly replaced by an emerald green one. After this time the excess ligand was removed by sublimation under reduced pressure. The procedure was then repeated with fresh 2-benzylaminopyridine to ensure complete exchange. The product was collected, washed with acetone, methanol and finally diethyl ether. It was dried under vacuum at 80 °C. Yield 0.40 g, 97%. *Anal.* Found: C, 59.5; H, 4.7; N, 11.4; Cl, 3.8. Calc. for $C_{48}H_{44}ClN_8Ru_2$: C, 59.4; H, 4.5; N, 11.5; Cl, 3.7%. Infrared spectrum (nujol mull, CsI plates): 1604(s), 1373(m), 1345(m), 1159(m), 1130(m), 824(s), 752(s), 728(s), 697(m), 522(m), 458(m), 383(m), 284(m) cm^{-1} (key: s, strong; m, medium). Magnetic moment (solid): $\mu_{eff} = 3.93$ BM at *ca.* 293 K. Electronic spectrum (400–900 nm, solid state diffuse reflectance): 482(br) and 748(br) nm.

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The complex is slightly soluble in dimethylsulphoxide but is insoluble in all other common organic solvents as well as in water.

$Ru_2(MeNpyr)_4Cl$

The complex $Ru_2(O_2CCH_3)_4Cl$ (0.2 g, 0.4 mmol) was placed in neat 2-(methylamino)pyridine (3 ml) and heated to 90 °C for four hours after which time the majority of the unreacted ligand had evaporated. A further sample of 2-(methylamino)pyridine (3 ml) was added and heating continued. After six hours any remaining unreacted ligand was removed under vacuum and the dark green residue collected and washed with ethanol, acetone, methanol and finally diethylether, prior to drying under vacuum at *ca.* 70 °C. Yield, 0.24 g, 85%. *Anal.* Found: C, 42.9; H, 4.2; N, 16.5; Cl, 5.4. Calc. for $C_{24}H_{28}ClN_8Ru_2$: C, 43.3; H, 4.2; N, 16.8; Cl, 5.3%. Infrared spectrum (nujol mull, CsI plates): 1600(s), 1531(w), 1376(m), 1288(m), 1163(m), 1123(m), 829(s), 746(s), 731(s), 638(m), 525(w), 453(w), 350(s), 304(m) cm^{-1}. Magnetic moment (solid): $\mu_{eff} = 4.36$ BM at *ca.* 293 K. Electronic spectrum (400–900 nm, solid state diffuse reflectance): 480(br) and 736(br) nm.

The complex is soluble in dimethylsulphoxide, slightly soluble in methylene chloride and acetonitrile, but insoluble in all other common organic solvents.

Instrumentation

Infrared spectra were recorded in the region 4000–250 cm^{-1} on a Perkin-Elmer 983 spectrophotometer using nujol mulls on caesium iodide plates. Magnetic measurements were made at *ca.* 293 K on a J.M.E. magnetic susceptibility balance. Diffuse reflectance spectra were recorded in the range 900–400 nm on a Pye Unicam SP1800 spectrophotometer. Raman spectra were recorded on a Spex 14018 spectrometer in conjunction with Coherent Radiation CR 3000 krypton and I70-4 argon ion lasers, using 647.10 nm and 514.53 nm lines respectively. Detection of scattered radiation was by standard photon counting techniques employing cooled RCA C31034 photomultipliers. All spectra were recorded at approximately 80 K using a Dewar assembly from samples of the complexes dispersed in KCl discs.

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 EA 441/5) and a Pt wire as the 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 XY recorder. Electrolyte solutions were 0.1 M in tetra-n-butylammonium tetrafluoroborate. Deaeration of the solution was performed before commencing the experiment and a stream of nitrogen was passed throughout. All potentials are reported with respect to the Ag/AgCl electrode, against which ferrocene is oxidised at a potential of +0.60 volts.

Results and Discussion

Preparation

Both compounds were prepared in high yield by reacting $Ru_2(O_2CCH_3)_4Cl$ with an excess of the appropriate ligand at elevated temperatures. This preparative route is particularly useful when the replaceable hydrogen is acidic enough to undergo exchange with the acetate bridging ligands of the starting material. The present complexes, **1** and **2**, are obtained using reaction conditions not dissimilar from those used to obtain **3** [6]. The products are obtained as green amorphous powders which are air stable for an indefinite period, and of very limited solubility. Elemental analyses (C, H, N, Cl) of both complexes are consistent with the formulations $Ru_2(MeNpyr)_4Cl$ and $Ru_2(PhCH_2Npyr)_4Cl$ (see 'Experimental'), for **1** and **2** respectively. The limited solubility of these compounds may imply that they are polymeric materials, like the ruthenium carboxylates [9–12] and amidates [5], rather than being discrete binuclear complexes, as is **3** [6]. Unfortunately all attempts to resolve this question have been unsuccessful due to our failure to obtain X-ray quality single crystals. However, it has already been demonstrated that meaningful comparisons may still be made between the properties of the binuclear, and the polymeric diruthenium(II½) complexes [6, 7, 13].

Vibrational Spectroscopy

The infrared spectra of both **1** and **2** are consistent with the quantitative replacement of all four acetates by $[MeNpyr]^-$ and $[PhCH_2Npyr]^-$, respectively. The absence of any bands above 3100 cm^{-1} in the spectrum of both complexes is consistent with the coordination of these ligands in the anionic form, and makes the presence of a neutral, axially bound molecule, such as was found in the complex $Ru_2(hp)_4Cl(Hhp)$ [6], unlikely. Each of the spectra contain strong bands at *ca.* 1600 cm^{-1} which can be assigned to the skeletal vibrations of the pyridyl rings. Strong bands at *ca.* 700–830 cm^{-1} in each of the spectra are also characteristic of each of the ligands. In the complex **3** the Ru–Cl stretching frequency has been assigned to a band at 311 cm^{-1} [6], and bands at 304 and 287 cm^{-1}, in **1** and

2 respectively, may be of similar origin. However, Drago has recently [14] pointed out that in the $Ru_2(O_2CR)_4Cl$ complexes the chlorides are bridging with a very long and thus weak Ru–Cl bond. Thus one would expect ν(Ru–Cl) to occur at a rather low frequency. Hence he assigned a strong absorption band at 195 cm^{-1} in the far-infrared spectrum of $Ru_2(O_2CC_3H_7)_4Cl$ to be ν(Ru–Cl). Medium to strong bands occur in the spectra of **1** and **2** in the region 350–450 cm^{-1} and it is likely that these may be $\nu(Ru-N_{am})$ and $\nu(Ru-N_{pyr})$ although the exact assignment is uncertain.

The ν(Ru–Ru) in the Raman spectra of the diruthenium carboxylates, $Ru_2(O_2CR)_4Cl$, has been observed at 327.3 cm^{-1}, for $R = CH_3$, and at 330.8 cm^{-1}, for $R = C_3H_7$, [15], however none of the more recently reported complexes has yet been studied in depth. Preliminary studies on **3**, have shown the presence of a strong band at 322 cm^{-1} in the Raman spectrum which may be assigned to the (Ru–Ru) stretching vibration [16]. The Raman spectra of **1** and **2** were recorded in the region 100–1400 cm^{-1}. The strongest band in each spectrum was at *ca.* 380 cm^{-1} however this would appear to be too high a frequency for ν(Ru–Ru). Medium intensity bands were observed at 344 and 346 cm^{-1}, in the spectrum of **1** and **2** respectively, and these would appear to be good candidates for the (Ru–Ru) stretching vibrations. A number of ligand-localised vibrations also occur in this region and therefore assignments based upon our brief survey of the Raman spectra of these complexes is not necessarily definitive.

Electronic and Magnetic Properties

The very low solubilities of these complexes has limited our study of the electronic spectra of **1** and **2** to the solid state. The diffuse reflectance spectrum of **1** exhibits two absorption bands, at 736 nm and 480 nm, while the spectrum of **2** contains absorption bands at 748 nm and 482 nm. The electronic spectrum of **3** has previously [6] been recorded in a CH_2Cl_2 solution. This spectrum contained two absorption bands, at 764 nm (ϵ 6910 M^{-1} cm^{-1}) and 415 nm (5770). All three spectra are remarkably similar and suggest that the transitions are of a similar origin. Unfortunately the theoretical calculations [17] so far carried out on the metal–metal bonded diruthenium complexes have been restricted to the much simpler carboxylates. These carboxylates exhibit absorption bands near 500 nm and SCF-Xα-SW calculations [17] have led to the assignment of this band to a $\pi(O) \rightarrow \pi^*(RuRu)$ transition. A further weak band at *ca.* 1000 nm has been assigned to the $\delta \rightarrow \delta^*$ transition [17]. The spectral features observed in compounds **1**–**3** are totally different from those of the carboxylates, and indeed those of the amidates, $Ru_2(R'NC(O)R)_4Cl$ [2–4], and without any theoretical treatment of the electronic structures of these new compounds any further discussion would be fruitless.

One of the most unusual features of the metal–metal bonded diruthenium(II½) complexes is their magnetic properties. The carboxylate complexes have been extensively investigated several times [8, 14, 18] and the results of every study have been consistent with the presence of three unpaired spins per binuclear unit. This result has been rationalised by SCF-Xα-SW calculations on $[Ru_2(O_2CH)_4]^+$ and its derivatives [17] which have shown that where there is strong Ru–Ru bonding a MO pattern results in which two π^* and one δ^* orbital are almost degenerate. This gives rise to the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$. Several 'one-off' measurements on the 'totally polar' complexes [6], and the amidates [2] have shown that at ambient temperatures these diruthenium(II½) complexes also exhibit a magnetic moment corresponding to three unpaired electrons. Magnetic measurements done on **1** and **2** in the solid state at *ca.* 293 K are also consistent with these observations (see 'Experimental') and indeed these values are in close agreement with that previously reported [6] for **3** ($\mu_{eff} = 3.94$ BM at 298 K, measured in CH_2Cl_2 solution by Evans' method, [19]). It is perhaps surprising that despite the wide variety of ligands which have now been shown to bridge the $Ru\overset{2.5}{\underline{\quad}}Ru$ bond the magnetic behaviour of these complexes has shown itself to be essentially invarient. Only when dealing with a non-bridged species, such as $[RuL]_2Cl$ (L = the dianion of dibenzotetraaza [14] annulene, $[C_{22}H_{22}N_4]^{2-}$) does the magnetic behaviour differ significantly [20].

Electrochemistry

The complex **1** was sufficiently soluble in dimethylsulphoxide for its redox behaviour to be studied by cyclic and a.c. voltammetry. In a solution containing 0.1 M $N(C_4H_9)_4BF_4$ as supporting electrolyte and no additional Cl^- ion there are three well defined responses between + 1.0 and – 1.5 V as shown in Fig. 1a. All potentials were measured against a Ag/AgCl reference electrode at *ca.* 295 K under an atmosphere of dinitrogen. The responses which appear between –0.6 and – 1.4 V are due to reduction while that at +0.24 V is an oxidation process.

The oxidation was observed at $E_{1/2} = +0.24$ V with a constant peak-to-peak separation (ΔE_p) of 80 mV over a range of scan rates. The anodic to cathodic peak current ratio, i_{pa}/i_{pc}, was unity at all scan rates; and therefore analyses closely as a reversible diffusion controlled process. The two quasi-reversible reductions were observed at $E_{1/2} = -0.78$ and – 1.11 V, with peak-to-peak separations of 120 and 160 mV respectively ($\nu = 50$ mV s^{-1}). It had previously been reported that complex **3** underwent a reversible

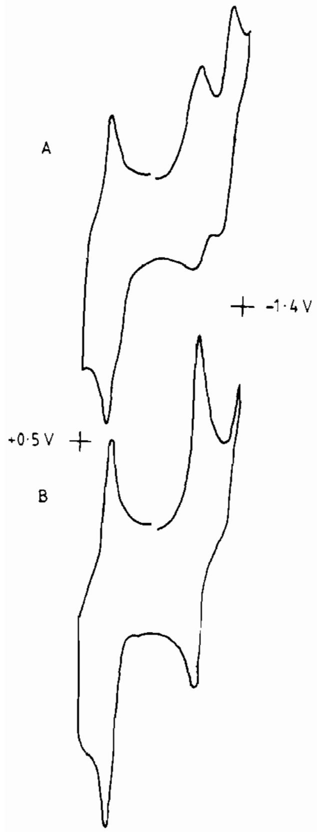

Fig. 1. Cyclic voltammagram of **1** in (a) Me_2SO (0.1 M $N((C_4H_9)_4BF_4)$ and (b) Me_2SO (0.1 M $N(C_4H_9)_4BF_4$ + 0.1 M $N(C_2H_5)_4Cl$. Scan rate = 100 mV s^{-1}. Potential, volts *vs.* Ag/AgCl.

oxidation and reduction, at +0.50 and −0.75 V respectively [13], and that further irreversible waves were observed in the cyclic voltammagram at −1.57 and +1.45 V. This shifting of potentials to more negative values or substituting a methyl group for a phenyl group, in $Ru_2(RNpyr)_4Cl$ complexes, corresponds, at least qualitatively, to an increase in the electron donicity of the bridging ligand on replacing $[PhNpyr]^-$ by $[MeNpyr]^-$, and therefore results in easier oxidations and more difficult reductions for **1**, compared with the corresponding processes of **3**. In the presence of an excess of Cl^- ion the cyclic voltammagram of **1** (see Fig. 1b) is simplified with a reversible oxidation now observed at +0.15 V ($\Delta E_p = 80$ mV) and a single reversible reduction now observed at −0.84 V ($\Delta E_p = 80$ mV). No second reduction wave being observed upto the solvent limit. Interestingly the shifts in potential with addition of Cl^- ion which were observed during studies of the electrochemistry of $Ru_2(HNC(O)CF_3)_4Cl$ [2] and $Ru_2(HNC(O)Ph)_4Cl$ [4], in dimethylsulphoxide, have no parallels in this study. However, the replacement of two reduction waves of similar potentials by a single reduction process is well documented [2, 18].

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