Synthesis, Spectroscopic, Electrochemical, and Magnetic Properties of Dimolybdenum(II,II), Diruthenium-(II,III) and -(II,II) Complexes containing Bridging Aspirinate (2-Acetoxybenzoate) Ligands

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Carboxylate exchange reactions were used to prepare the dimolybdenum(II,II) tetra-aspirinate complex, $[Mo_2(\mu\text{-asp})_4]$ (**1**), and the soluble aspirinate/trifluoroacetate, $[Mo_2(\mu\text{-asp})(\mu\text{-}O_2CCF_3)_3]\cdot 2H_2O$ (**2**) (asp = aspirinate = 2-acetoxybenzoate). Similar metathesis reactions were used for the synthesis of the diruthenium(II,III) complexes, $[Ru_2(\mu\text{-asp})_4Cl]$ (**3**), $[Ru_2(\mu\text{-asp})_2(\mu\text{-}O_2CC_6H_5)_2Cl]\cdot H_2O$ (**4**), and $[Ru_2(\mu\text{-asp})_4(O_2CCF_3)]\cdot 2H_2O$ (**5**). A methanolic solution of (**3**) reacts with an aqueous solution of $AgNO_3$ at 20 °C to give the Ru_2^{5+} nitrate/aspirinate, $[Ru_2(asp)_4(NO_3)]\cdot H_2O$ (**6**). When this reaction is repeated at 70 °C the Ru_2^{4+} nitroso/aspirinate, $[Ru_2(asp)_4(NO)]\cdot 4H_2O$ (**7**), is isolated. Complex (**7**) also formed when a methanolic solution of (**6**) was either refluxed (70 °C) for 3 h, or allowed to stand (20 °C) for a period of 3—4 weeks. The conversion of (**3**) and (**6**) into (**7**) represents a reduction of both the bimetallic core (Ru_2^{5+} to Ru_2^{4+}) and the nitrate group (NO_3^- to NO). Infrared absorption spectra, conductivity, cyclic voltammetry, and magnetic susceptibility data are given.

Lately there has been a lot of interest in the therapeutic properties of bimetallic carboxylate complexes. It has been established that certain tetra-μ-carboxylato-dirhodium(II,II) carboxylates function as antitumour agents against many types of tumour by inhibiting DNA and protein synthesis.[1,2] More recently, Sorenson and his co-workers demonstrated that in tests on mice diaquatetra-μ-di-3,5-isopropylsalicylato-dicopper(II,II) afforded significant protection against radiation damage to cells by effectively scavenging superoxide.[3] Also, following the preparation of tetra-μ-aspirinato-dicopper(II,II), $[Cu_2(\mu\text{-asp})_4]$ (asp = aspirinate = 2-acetoxybenzoate),[4] it was soon discovered that the complex was a very effective anti-inflammatory agent.[5]

In this paper we describe the synthesis and properties of some dimolybdenum(II,II) and diruthenium(II,III) aspirinate complexes. In addition, the temperature-controlled preparations of a diruthenium(II,III) nitrato/aspirinate complex and a diruthenium(II,II) nitroso/aspirinate complex are also described.

Results and Discussion

Tetra-μ-aspirinato-dimolybdenum(II,II) (**1**) *and μ-Aspirinato-tris(μ-trifluoroacetato)-dimolybdenum*(II,II) *Dihydrate* (**2**).—Carboxylate-exchange reactions for the preparation of $[Mo_2(\mu\text{-asp})_4]$ (**1**) and $[Mo_2(\mu\text{-asp})(\mu\text{-}O_2CCF_3)_3]\cdot 2H_2O$ (**2**) are shown in Scheme 1. Although complex (**1**) was treated with excess of trifluoroacetic acid only three of the four aspirinate groups were substituted by trifluoroacetates giving the mixed-carboxylate complex, (**2**). The i.r. spectral data (Table 1) suggest that the aspirinate ligands in both complexes are bridging bidentate, and that the three trifluoroacetate ligands in (**2**) are also bridging bidentate {*cf.* i.r. data for $[Mo_2(\mu\text{-}O_2CCF_3)_4]$}. The spectrum of (**1**) contained two ν(C=O)(acetyl) bands at frequencies similar to those reported for $[Cu_2(\mu\text{-asp})_4]$[6] (Table 1). The crystal structure of $[Cu_2(\mu\text{-asp})_4]$[4] showed that some of the acetyl oxygens were used to form intermolecular bridges to the axial sites of neighbouring bimetallic units, and individual ν(C=O) bands were observed for the bonded and non-bonded acetyl groups. The aspirinate ligand is too short to allow the acetyl oxygen to form an intramolecular bond to one of the two molybdenums to which its own carboxylate group is already bonded to. The spectrum of the structurally characterized mononuclear complex $[Cu(asp)_2(py)_2]$ (py = pyridine)[7] contained only a single acetyl ν(C=O) band corresponding to the non-bonded acetyl groups of the two chelating aspirinate ligands. Thus, complex (**1**) is believed to be isostructural with $[Cu_2(\mu\text{-asp})_4]$. The spectrum of complex (**2**) contained only one acetyl ν(C=O) band at 1 655 cm^{-1} and the low-frequency position of this band suggests that the acetyl oxygen of the single aspirinate ligand is strongly bonded to a molybdenum in a neighbouring bimetallic unit.

$$\begin{tikzcd}
 & {[Mo_2(\mu\text{-}O_2CC_6H_5)_n(\mu\text{-}O_2CCH_2OCH_3)_{4-n}]\ (n = 0\text{—}4)} \arrow[d, "(ii)"'] \\
{[Mo_2(\mu\text{-}O_2CR)_4]} \arrow[r, "(i)"] & {[Mo_2(\mu\text{-asp})_4]\ (1)} \arrow[d, "(iii)"'] \\
 & {[Mo_2(\mu\text{-asp})(\mu\text{-}O_2CCF_3)_3]\cdot 2H_2O\ (2)}
\end{tikzcd}$$

Scheme 1. (*i*) Hasp; R = CH_3 or C_6H_5; (*ii*) Hasp; (*iii*) CF_3CO_2H

In dimethylformamide (dmf) $[Mo_2(\mu\text{-asp})_4]$ (**1**) was found to be electroinactive in the potential region 100 to −1 000 mV [Figure 1(*a*)]. In the range 100—1 200 mV a broad, irreversible oxidation peak (A) was observed [Figure 1(*b*)]. When the potential sweep was extended to cover the range 1 200 to −1 000 mV the irreversible oxidation peak (A) was present along with the redox couple (BC) [Figure 1(*c*)]. It is evident that the redox couple (BC) is a feature of the oxidized product(s) arising from the irreversible oxidation of complex (**1**) (peak A) and that what we are seeing is a coupled chemical reaction of the e.c.e. type (*i.e.* an electron transfer step followed by a chemical reaction step followed by another electron transfer step). From a study of the effects of scan rate on the profile of the voltammogram (1 200 to −1 000 mV) of complex (**1**) (Table 2) a number of trends were observed. (*i*) ΔE_p was >59 mV at all scan rates (ν), and, with the exception of ν = 100 mV

Table 1. Selected i.r. data (cm^{-1}) for the complexes

	asp$^-$			$O_2CC_6H_5$		O_2CCF_3		NO_3^- [a]	NO
Complex	ν(C=O)(acetyl)	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\nu(NO_2)$	ν(NO)
$[Mo_2(asp)_4]$ (**1**)	1 760, 1 740	1 510	1 400						
$[Mo_2(asp)(\mu\text{-}O_2CCF_3)_3]\cdot 2H_2O$ (**2**)	1 655	1 490	1 390			1 600	1 460		
$[Ru_2(asp)_4Cl]$ (**3**)	1 765	1 480	1 400						
$[Ru_2(asp)_2(\mu\text{-}O_2CC_6H_5)_2Cl]\cdot H_2O$ (**4**)	1 765	1 480	1 400	*b*					
$[Ru_2(asp)_4(O_2CCF_3)]\cdot 2H_2O$ (**5**)	1 765	1 480	1 400			1 680	*c*		
$[Ru_2(asp)_4(NO_3)]\cdot H_2O$ (**6**)	1 760	1 480	1 400					1 290	
$[Ru_2(asp)_4(NO)]\cdot 4H_2O$(**7**)	1 760	1 480	1 400						1 875
(**8**)								1 380, 820	
(**9**)								1 380, 1 285, 825	1 890
(**10**)								1 380, 1 285, 825	1 890
$[Mo_2(\mu\text{-}O_2CCF_3)_4]$ [d]						1 600	1 460		
$[Ru_2(\mu\text{-}O_2CC_6H_5)_4Cl]$ [e]				1 470	1 410				
$[Ru_2(\mu\text{-}O_2CC_6H_5)_4(O_2CCF_3)]\cdot 2H_2O$ [f]				1 470	1 410	1 680			
$[Cu_2(asp)_4]$ [g]	1 760, 1 729	1 620	1 410						
$[Cu(asp)_2(py)_2]$ [h]	1 748	1 603	1 405						
Hasp	1 755	1 690 (carboxyl C=O)							

[a] The nitrate high energy $\nu_{asym}(NO_2)$ band which usually appears around 1 420 cm^{-1} (see ref. 12) is masked by the strong $\nu_{sym}(CO_2)$ band of the carboxylate groups. [b] $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands for the benzoate ligands are directly overlapped by the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands of the aspirinate ligands. [c] The $\nu_{sym}(CO_2)$ band of the trifluoroacetate group is overlapped by the aspirinate $\nu_{sym}(CO_2)$ band. [d] See F. A. Cotton and J. G. Norman, *J. Coord. Chem.*, 1971, **1**, 161. [e] See ref. 13. [f] See ref. 9. [g] See ref. 6. [h] See ref. 7.

Table 2. Voltammetry measurements for $[Mo_2(\mu\text{-asp})_4]$ (**1**) as a function of scan rate[a]

Scan rate/ mV s^{-1}	Irreversible oxidation peak (A)[b]/mV	E_{pc}(B)/mV	E_{pa}(C)/mV	ΔE_p/mV	$E_{\frac{1}{2}}$/mV	i_{pc}/μA	i_{pa}/μA	i_{pc}/i_{pa}
50	385	−418	−341	77	−380	4.89	2.11	2.31
100	397	−428	−296	132	−327	7.61	4.70	1.62
200	415	−396	−292	104	−344	10.23	7.56	1.35
500	436	−387	−270	117	−329	15.16	13.71	1.11
1 000	426	−384	−243	141	−315	18.53	20.39	0.91

[a] The solution was 1.0 mmol dm^{-3} in dmf, and the potential range scanned was 1 200 to −1 000 mV; in dmf the ferrocene–ferrocenium couple had $E_{\frac{1}{2}}$ = 498mV. [b] Potential for the onset of the broad, irreversible oxidation peak (A).

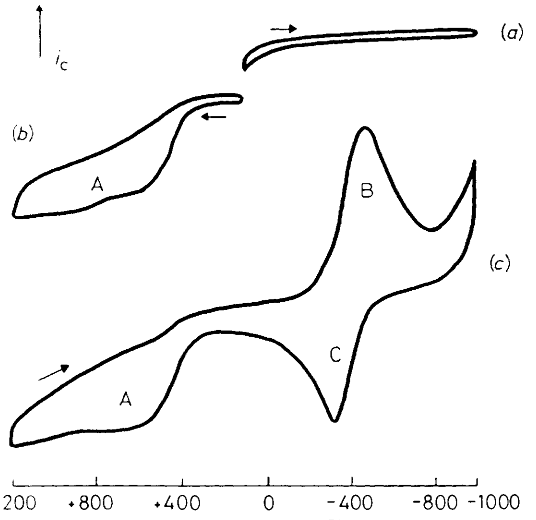


Figure 1. Cyclic voltammograms of the Mo_2^{4+} complex (**1**) (1.0 mmol dm^{-3} in dmf) in the potential regions (*a*) 100 to −1 000, (*b*) 100 to 1 200, and (*c*) 1 200 to −1 000 mV. Scan rate = 100 mV s^{-1}

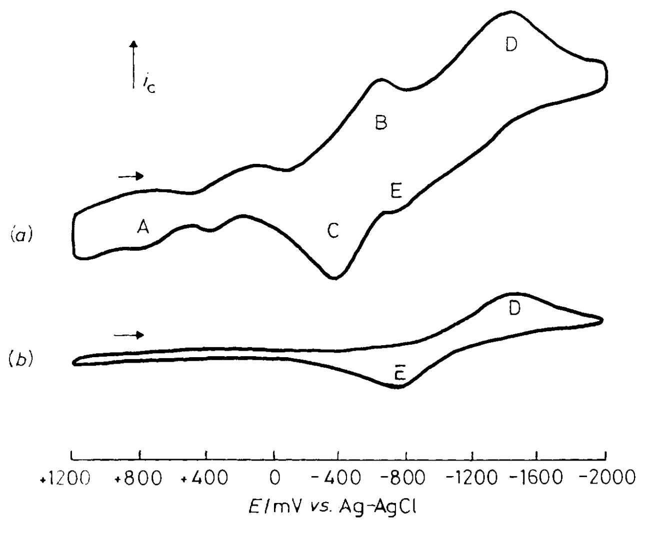


Figure 2. Cyclic voltammograms of (*a*) complex (**1**) and (*b*) Hasp in the potential region 1 200 to −1 000 mV. Solutions were 1.0 mmol dm^{-3} in dmf (scan rate = 100 mV s^{-1})

s^{-1}, ΔE_p increased as ν increased. (*ii*) E_{pc}(B) did not vary much with changes in ν. (*iii*) E_{pa}(C) only shifted slightly to more positive potentials on increasing ν. (*iv*) i_{pc} and i_{pa} were proportional to $\nu^{\frac{1}{2}}$. (*v*) i_{pc}/i_{pa} for BC was $\geqslant 1$ at the lower scan rates. (*vi*) i_{pc}/i_{pa} for BC approached a value of unity at the higher scan rates. Whilst trends (*ii*)—(*iv*), and (*vi*) indicated that the couple BC might be reversible, (*i*) and (*v*) suggested that it was quasireversible. These contrasting trends concerning the reversibility of the couple BC are, presumably, a consequence of the nature of the coupled chemical reaction occurring at the working electrode. The electrochemical behaviour of complex (**1**) is summarized in Scheme 2 and we have indicated that the oxidized product(s) may fragment into mono- or poly-nuclear complexes. Experiments are currently in progress to establish the identity of the oxidized product(s).

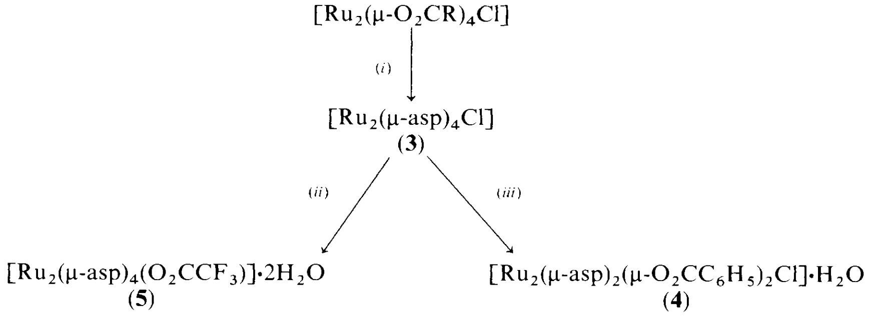
$$Mo_2^{4+} \xrightarrow{-ne} Mo_w^{x+} \longrightarrow Mo_y^{z+} \underset{-e}{\overset{+e}{\rightleftharpoons}} Mo_y^{(z-1)+}$$

Scheme 2. $w \geqslant 1, y \geqslant 1$

When the potential range scanned was extended to cover 1 300 to −2 000 mV two further peaks (D and E) appeared [Figure 2(*a*)]. These two new peaks are thought to be due to the respective reduction and oxidation of un-coordinated aspirinate groups. Two similar peaks were observed when the voltammogram of Hasp was recorded in dmf [Figure 2(*b*)].

The electrochemical behaviour of (**1**) in dmf was very different to that reported for solutions of $[Mo_2(\mu\text{-}O_2CC_3H_7)_4]$ in acetonitrile, dichloromethane, and ethanol.[8] The butyrate showed a quasireversible, one-electron oxidation (Mo_2^{4+}/Mo_2^{5+}) in CH_3CN [$E_{\frac{1}{2}}$ = 390 mV *vs.* saturated calomel electrode (s.c.e.)], CH_2Cl_2 ($E_{\frac{1}{2}}$ = 450 mV), and C_2H_5OH ($E_{\frac{1}{2}}$ = 300 mV). We believe that the differences in the voltammograms of the butyrate and the aspirinate (**1**) are primarily due to the use of dmf as solvent for the latter species. We recorded the voltammogram of $[Mo_2(\mu\text{-}O_2CCH_3)_4]$ in methanol and found the behaviour to be similar to that reported for the butyrate, *i.e.* quasireversible, one-electron oxidation ($E_{\frac{1}{2}}$ = 239 mV *vs.* Ag–AgCl). However, the voltammogram of $[Mo_2(\mu\text{-}O_2CCH_3)_4]$ in dmf was similar to that shown in Figure 2(*a*) above, *i.e.* an irreversible oxidation peak (A) and a reversible/quasireversible redox couple (BC). We did not record the voltammogram of the butyrate complex in dmf.

Tetra-μ-aspirinato-chlorodiruthenium(II,III) (**3**), *Di-μ-aspirinato-di-μ-benzoato-chlorodiruthenium*(II,III) *Hydrate* (**4**), *Tetra-μ-aspirinato-trifluoroacetatodiruthenium*(II,III) *Dihydrate* (**5**), *Tetra-μ-aspirinato-nitratodiruthenium*(II,III) *Hydrate* (**6**), *and Tetra-μ-aspirinato-nitrosyldiruthenium*(II,II) *Tetrahydrate* (**7**).—Scheme 3 summarizes the synthetic routes to the Ru_2^{5+} complexes, $[Ru_2(\mu\text{-asp})_4Cl]$ (**3**), $[Ru_2(\mu\text{-asp})_2(\mu\text{-}O_2CC_6H_5)_2Cl]\cdot H_2O$ (**4**), and $[Ru_2(\mu\text{-asp})_4(O_2CCF_3)]\cdot 2H_2O$ (**5**). The reaction of $[Ru_2(\mu\text{-}O_2CR)_4Cl]$ (R = CH_3 or C_6H_5) with excess of Hasp gave the fully substituted chlorotetra-aspirinate, (**3**). Complex (**3**) is believed to be isostructural with the parent chlorotetracarboxylates, and its i.r. spectrum contained asymmetric and symmetric $\nu(CO_2)$ bands for the bridging bidentate aspirinate ligands at 1 480 and 1 400 cm^{-1}, respectively (Table 1). Complex (**3**) reacted with benzoic acid



Scheme 3. (*i*) Hasp; R = CH_3 or C_6H_5; (*ii*) $Ag(O_2CCF_3)$; (*iii*) $C_6H_5CO_2H$

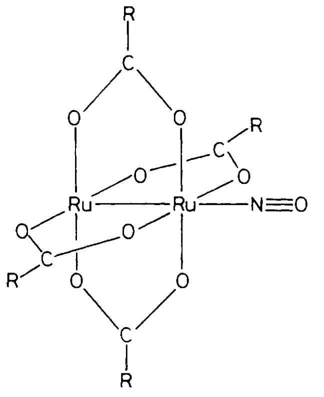


Figure 3. Proposed structure of $[Ru_2(\mu\text{-asp})_4(NO)]\cdot 4H_2O$ (**7**) (water molecules not shown)

(*ca.* 1:2 molar ratio) to give the orange, disubstituted product, (**4**). By comparing the i.r. spectrum of (**4**) with the spectra of (**3**) and $[Ru_2(\mu\text{-}O_2CC_6H_5)_4Cl]$ it is clear that the four carboxylate groups in (**4**) are co-ordinated in a bridging bidentate fashion. The reaction of a methanolic solution of (**3**) with silver trifluoroacetate (1:1 molar ratio) led to the precipitation of the stoicheiometric amount of silver chloride and subsequent isolation of the monotrifluoroacetate complex, (**5**). The i.r. spectrum of (**5**) suggests that the aspirinate ligands are bridging bidentate and that the trifluoroacetate group is ionic.[9] The spectra of complexes (**3**)—(**5**) had only a single high-frequency ν(C=O)(acetyl) band indicating that the acetyl oxygens were probably not bonded to a neighbouring Ru_2 unit.

Routes to the Ru_2^{5+} nitrate/aspirinate (**6**) and the Ru_2^{4+} nitroso/aspirinate (**7**) are shown in Scheme 4. The orange complex (**6**) was made by treating a methanolic solution of the respective chloro complex, (**3**), with an aqueous solution of silver nitrate (1:1 molar ratio) at 20 °C. The i.r. spectrum of (**6**) had bands attributable to both the nitrate and the aspirinate groups (Table 1), and the position of the $\nu_{sym}(NO_2)$ band (1 290 cm^{-1}) was very similar to that reported for the nitrate group in $[Ru_2(\mu\text{-}O_2CCH_3)_4(NO_3)]$ (1 288 cm^{-1}).[10,*]

When the above reaction was repeated at 70 °C the dark brown, Ru_2^{4+} mononitroso complex, (**7**), was isolated. Complex (**7**) also formed when a methanolic solution of (**6**) was either refluxed (70 °C) for 3 h, or allowed to stand (20 °C) for a period of 3—4 weeks. No reduction of NO_3^- to NO was observed during the preparation of $[Ru_2(\mu\text{-}O_2CCH_3)_4(NO_3)]$.[10] The complex was made by passing a solution of $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ in dilute acetic acid through an anion (NO_3^-) exchange column. Potassium nitrate was added to the eluate, and the resulting solution was then concentrated on a water-bath to give the brown, crystalline product. Although the authors did not specify any reaction temperatures it is assumed that some heating was required (*i*) to get the $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ to dissolve in the dilute acetic acid, and (*ii*) to concentrate the solution on the water-bath. The conversion of (**6**) into (**7**) was seen by the loss of the nitrate band at 1 290 cm^{-1} and the presence of a medium-strength, broad ν(NO) band at 1 875 cm^{-1} in the i.r. spectrum of (**7**). For the bis-nitroso complexes, $[Ru_2(\mu\text{-}O_2CR)_4(NO)_2]$ (R = Me, Et, Ph, or CF_3),[11] one and sometimes two ν(NO) bands appeared in the region 1 722—1 800 cm^{-1}, implying linear Ru–N–O linkages. However, this interpretation was contradicted by the *X*-ray structural data for the trifluoroacetate and propionate complexes, which showed the Ru–N–O angles to be *ca.* 153° in each case. The fact that the ν(NO) band of (**7**) appeared some 75 cm^{-1} to higher energy than the highest-energy band for the $[Ru_2(\mu\text{-}O_2CR)_4(NO)_2]$ complexes suggests that the Ru–N–O moiety in (**7**) may indeed be linear.[12] Complex (**7**) functioned as a weak electrolyte in methanol, and the proposed structure of the complex is shown in Figure 3.

Whereas complexes (**4**)—(**6**) behave as 1:1 electrolytes in methanol their precursor, (**3**), is essentially undissociated in that solvent. The magnetic moments of complexes (**3**)—(**6**) were similar to those quoted for other Ru_2^{5+} (d^{11}) complexes, and consistent with species containing three unpaired electrons per Ru_2 unit.[10,13] The magnetic moment of (**7**) was similar to that reported for the Ru_2^{4+} (d^{12}) tetracarboxylates, $[Ru_2(\mu\text{-}O_2CR)_4]$ (R = H, Me, CH_2Cl, Et, or Ph), and their weakly end-co-ordinated bis adducts, $[Ru_2(\mu\text{-}O_2CR)_4L_2]$ [L = H_2O, tetrahydrofuran (thf), Me_2CO, or MeCN].[14] In these complexes the moments translated to two unpaired electrons per molecule, *i.e.* a triplet ground state ($\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$). However, the paramagnetism of (**7**) contrasts with the diamagnetism of the formally Ru_2^{2+} (d^{14}) bis-nitroso complexes, $[Ru_2(\mu\text{-}O_2CR)_4(NO)_2]$, which have the spin-paired configuration, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ (or $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$).[11] It should be emphasized that in these complexes the two nitroso ligands were formally regarded as nitrosonium ions (NO^+), each of the two NO molecules having used their single π* electron to reduce the bimetallic core from Ru_2^{4+} (d^{12}) to Ru_2^{2+} (d^{14}). Applying the same electron-counting argument to (**7**) would give an Ru_2^{3+}

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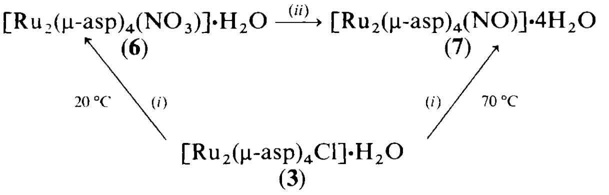
[*] The i.r. spectrum of $[Ru_2(\mu\text{-}O_2CCH_3)_4(NO_3)]$ contained bands for the nitrate group at 1 388, 1 288, and 809 cm^{-1}, and the position of these three bands was taken to indicate that the nitrate group was present as a co-ordinated ligand.[10] Only a single nitrate band (1 290 cm^{-1}) was observed in the spectrum of (**6**), and this is probably due to the masking of the high- and low-energy bands by aspirinate bands which also occur in these regions. Thus, at present we are uncertain as to the co-ordination mode of the nitrate group in (**6**) in the solid state.

Table 3. Voltammetry measurements for the diruthenium complexes (**3**), (**6**), and (**7**)*

Complex	Scan rate/ mV s^{-1}		E_{p_c}/mV	E_{p_a}/mV	ΔE_p/mV	$E_{\frac{1}{2}}$/mV	i_{p_c}/i_{p_a}	Comments
[Ru$_2$(μ-asp)$_4$Cl] (**3**)	100	(i)	70	218	148	144	1.5	Quasireversible
		(ii)	−398	No anodic peak				Irreversible
[Ru$_2$(μ-asp)$_4$(NO$_3$)]·H$_2$O (**6**)	200		77	173	96	125	1.1	Reversible
[Ru$_2$(μ-asp)$_4$(NO)]·4H$_2$O (**7**)	200	(i)	123	175	52	149	1.0	Reversible
		(ii)	37	No anodic peak				Irreversible

* All solutions were 1.0 mmol dm^{-3} in MeOH, and the potential range scanned was 400 to −1 500 mV.



Scheme 4. (*i*) AgNO$_3$(aq), CH$_3$OH; (*ii*) CH$_3$OH, 20 or 70 °C

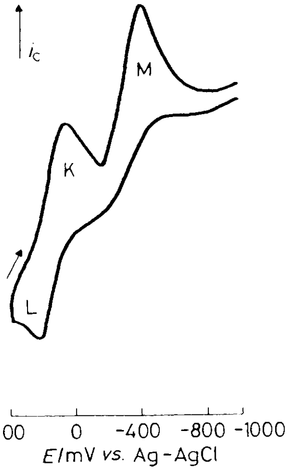


Figure 4. Cyclic voltammogram of [Ru$_2$(μ-asp)$_4$Cl] (**3**) (scan rate = 100 mV s^{-1})

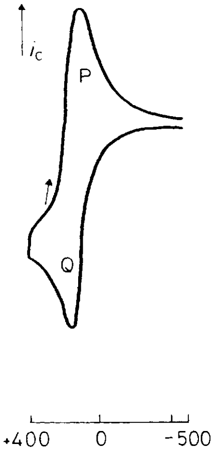


Figure 5. Cyclic voltammogram of [Ru$_2$(μ-asp)$_4$(NO$_3$)]·H$_2$O (**6**) (scan rate = 200 mV s^{-1})

(d^{13}) core for the complex. However, using the metal–metal bonding scheme of Norman *et al.*[15] ($\sigma\ \pi\ \delta\ \delta^*\ \pi^*\ \sigma^*$) it is not possible to write a logical electronic configuration for (**7**) which would give two unpaired electrons per molecule. For the present time we think that it is simplest to consider (**7**) as an Ru$_2^{4+}$ complex (NO present as a neutral ligand), with the resultant magnetic moment of the complex arising from the coupling of unpaired metal electrons with the NO π^* electron. This situation again highlights the difficulties that arise when formal charges are assigned to individual atoms in a complex.[11]

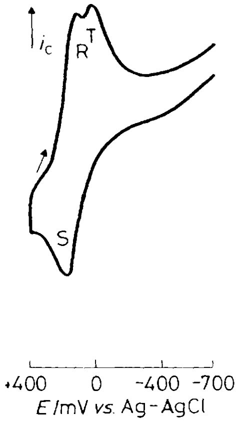


Figure 6. Cyclic voltammogram of [Ru$_2$(μ-asp)$_4$(NO)]·4H$_2$O (**7**) (scan rate = 200 mV s^{-1})

Voltammograms of the Ru$_2^{5+}$ complexes (**3**) and (**6**) are shown in Figures 4 and 5, respectively, and the potential measurements are given in Table 3. The chloro/aspirinate (**3**) had a quasireversible, one-electron redox couple (KL) and an irreversible one-electron peak (M).* The voltammogram of (**3**) is very similar to that reported for the Ru$_2^{5+}$ complex, [Ru$_2$(O$_2$CCH$_3$)$_2$(O$_2$CCF$_3$)$_3$(H$_2$O)$_{0.5}$],[9] and the behaviour of the complex is summarized in Scheme 5. In contrast, the voltammogram of the nitrate/aspirinate (**6**) contained only a single, reversible, one-electron couple (Ru$_2^{5+}$–Ru$_2^{4+}$) (PQ) the $E_{\frac{1}{2}}$ value of which was similar to that of the couple KL. The presence of a single redox couple for (**6**) is similar to that observed for some other Ru$_2^{5+}$ carboxylates.[9,17] As yet we cannot offer an explanation as to why only some Ru$_2^{5+}$ carboxylates have both a reversible (or quasireversible) redox couple and an irreversible reduction peak in their h.m.d.e. cyclic voltammograms.

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* From an analysis of the geometry of the irreversible reduction peak (M) (using the method outlined in ref. 9) it was found that this peak corresponded to a one-electron transfer. We also recorded the voltammograms of (**3**) and (**6**) using a platinum disc working electrode (scan rate = 500 mV s^{-1}, and potential scan range 800 to −1 100 mV). The voltammogram of (**6**) was similar to that obtained at the hanging mercury drop electrode (h.m.d.e.), with $E_{\frac{1}{2}}$ = 38 mV for the single redox couple. Whereas (**3**) exhibited both a quasireversible and an irreversible reduction peak at the h.m.d.e. (Figure 4), only a single, reversible redox couple was observed at Pt, with $E_{\frac{1}{2}}$ = 13 mV. The different behaviour of an electroactive species at different electrode surfaces is a well known phenomenon.[16]

$$Ru_2{}^{5+} \underset{-e}{\overset{+e}{\rightleftharpoons}} Ru_2{}^{4+} \xrightarrow{+e} \text{decomposition products}$$

Scheme 5.

The voltammogram of the $Ru_2{}^{4+}$ mononitroso/aspirinate (**7**) (Figure 6) shows a reversible, one-electron redox couple (RS) ($E_{\frac{1}{2}}$ = 149 mV) and an irreversible, one-electron reduction peak (T) (E_c = 37 mV). It seems likely that the redox couple giving rise to peaks R and S is not an $Ru_2{}^{4+}$–$Ru_2{}^{3+}$ couple as one would expect the $E_{\frac{1}{2}}$ value for this couple to be at a much more negative potential than the $E_{\frac{1}{2}}$ value for the $Ru_2{}^{5+}$–$Ru_2{}^{4+}$ couple in the voltammogram of (**6**) ($E_{\frac{1}{2}}$ = 125 mV). It is thought that at the initial potential of 400 mV (*vs.* Ag–AgCl) (**7**) has already been electrochemically oxidized to the $Ru_2{}^{5+}$ state, and that peaks R and S represent the $Ru_2{}^{5+}$–$Ru_2{}^{4+}$ couple. Thus, peak T corresponds to the irreversible reduction of the $Ru_2{}^{4+}$ complex [*i.e.* Scheme 5 can be used to represent the electrochemical behaviour of (**3**) and (**7**)]. The $Ru_2{}^{2+}$ bis-nitroso/propionate, $[Ru_2(\mu\text{-}O_2CC_2H_5)_4(NO)_2]$, exhibited a reversible $Ru_2{}^{3+}$–$Ru_2{}^{2+}$ couple at $E_{\frac{1}{2}}$ = 1 200 mV (*vs.* s.c.e.) and an irreversible reduction at −860 mV (platinum working electrode).[11]

Wilkinson and his co-workers[11] prepared the series of bis-nitroso $Ru_2{}^{2+}$ complexes of formula $[Ru_2(\mu\text{-}O_2CR)_4(NO)_2]$ by treating the respective $Ru_2{}^{4+}$ complexes, $[Ru_2(\mu\text{-}O_2CR)_4]$, with nitrogen monoxide at ambient temperature. However, the facile thermal conversion of complexes (**3**) and (**6**) into (**7**) represents a reduction of $NO_3{}^-$ to NO with concomitant reduction of the bimetallic core ($Ru_2{}^{5+}$ to $Ru_2{}^{4+}$).* The dual reduction ($Ru_2{}^{5+}$ to $Ru_2{}^{4+}$, and $NO_3{}^-$ to NO) which occurs in the synthesis of (**7**) from (**3**) and (**6**) is similar to that which occurs in the preparation of the tetranuclear platinum(II) nitroso/acetate, $[Pt_4(\mu\text{-}O_2CCH_3)_6(\mu\text{-}NO)_2]\cdot 2CH_3CO_2H$.[18] This complex was prepared by the reduction of a platinum(IV) species in nitric acid–acetic acid. Although $NO_3{}^-$ to NO reductions have been effected using certain complexes of Mo^V,[19] Ni^{II},[20] and Re^V,[21] the above reaction is the first authenticated example for a diruthenium complex. It has previously been reported that the treatment of a hot methanolic solution of $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ with the stoicheiometric amount of silver nitrate, and with subsequent addition of HBF_4 and PPh_3, leads to the formation of a ruthenium nitroso species (the complex itself was not isolated).[22]

The effect of temperature on product formation was further exemplified by the reactions of $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ with concentrated nitric acid. The i.r. spectrum of complex (**8**) (precipitate from the room-temperature reaction) contained only nitrate bands, whilst the spectrum of (**9**) (tarry residue remaining after evaporating the filtrate to dryness at 100 °C) had bands attributable to the presence of both nitrate and nitrosyl groups (Table 1). Furthermore, reaction of '$RuCl_3\cdot 3H_2O$' with silver nitrate in hot nitric acid ultimately gave a product, (**10**), the spectrum of which was identical to that of (**9**). In addition, temperature-controlled experiments have been used successfully to prepare mononuclear ruthenium nitrate and nitroso complexes.[23] For example, $[Ru(NO_3)_2(CO)(PPh_3)_2]$ and $[Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)]$ were isolated from the reaction between $[RuH_2(CO)(PPh_3)_3]$ and 16 mol dm^{-3} HNO_3 at 0 and 97 °C, respectively.[24]

Finally, the treatment of the ruthenium dioxygen/nitroso complex $[Ru(O_2)(NO)(PPh_3)_2Cl]$ with CO to give the nitrate complex $[Ru(NO_3)(PPh_3)_2(CO)_2Cl]$ represents an intramolecular oxidation of co-ordinated NO by co-ordinated O_2.[25] This oxidation (NO to $NO_3{}^-$) is effectively the reverse of what happens when complexes (**3**) and (**6**) are reduced to (**7**) ($NO_3{}^-$ to NO).

Experimental

Except where specified all chemicals were reagent grade and were used without further purification. Elemental analyses were performed by the Microanalytical Laboratory, University College Cork, Ireland. Infrared spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 783 grating spectrometer, and solid-state, room-temperature magnetic susceptibility measurements were made on a Johnson Matthey magnetic susceptibility balance. Cyclic voltammograms (*ca.* 20 °C and under N_2) were recorded using an EG&G model 264A polarographic analyser in combination with an EG&G PARC model 303 electrode assembly. A platinum disc was used as a working electrode for the molybdenum complex, and a hanging mercury drop electrode (h.m.d.e.) for the ruthenium complexes. A platinum wire was used as the auxiliary electrode and potentials (mV) were recorded with respect to a silver–silver chloride reference electrode. Tetraethylammonium perchlorate (70 mmol dm^{-3}) was used as the supporting electrolyte, and dry methanol and dry dmf were used as solvents for the ruthenium and molybdenum complexes, respectively. Voltammetry data for the molybdenum complex were analysed with the aid of the EG&G Condecon (TM) 300 system. Conductivities (1.0 mmol dm^{-3} solutions in methanol) were measured using an AGB Scientific Ltd. model 10 conductivity meter.

Literature methods were used to prepare $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$,[26] $[Ru_2(\mu\text{-}O_2CC_6H_5)_4Cl]$,[9] $[Mo_2(\mu\text{-}O_2CCH_3)_4]$,[27] $[Mo_2(\mu\text{-}O_2CC_6H_5)_4]$,[28] and $[Mo_2(\mu\text{-}O_2CC_6H_5)_n(\mu\text{-}O_2CCH_2OCH_3)_{4-n}]$ (n = 0—4).[29] Samples (**8**)—(**10**) were not isolated in a pure form.

$[Mo_2(\mu\text{-asp})_4]$ (**1**).—*Method* 1. The complex $[Mo_2(\mu\text{-}O_2CCH_3)_4]$ (0.30 g, 0.70 mmol), Hasp (1.01 g, 5.60 mmol), and dry methanol (20 cm^3) were refluxed under N_2 for 4 h. The orange product gradually precipitated over this time. After cooling under N_2 the solid was filtered off, washed with methanol, and dried *in vacuo*. Yield: 0.38 g (60%). Note: (**1**) was the only product isolated when the reaction was carried out with a 1 : 2 molar ratio of $[Mo_2(\mu\text{-}O_2CCH_3)_4]$: Hasp.

Method 2. The reaction time and reactant ratios were the same as in Method 1 except that $[Mo_2(\mu\text{-}O_2CC_6H_5)_4]$ was used instead of $[Mo_2(\mu\text{-}O_2CCH_3)_4]$.

Method 3. The complex $[Mo_2(\mu\text{-}O_2CC_6H_5)_n(\mu\text{-}O_2CCH_2OCH_3)_{4-n}]$ (n = 0—4) (0.10 g), Hasp (0.06 g, 0.33 mmol), and dry methanol (15 cm^3) were refluxed under N_2 for 4 h. Precipitation and recovery of the product was as specified in Method 1. Complex (**1**) was insoluble in all common solvents except dimethylformamide (Found: C, 46.95; H, 3.20. Calc. for $C_{36}H_{28}Mo_2O_{16}$: C, 47.60; H, 3.10%).

$[Mo_2(\mu\text{-asp})(\mu\text{-}O_2CCF_3)_3]\cdot 2H_2O$ (**2**).—Complex (**1**) (0.20 g, 0.22 mmol), trifluoroacetic acid (7 cm^3), and trifluoroacetic anhydride (2 cm^3) were refluxed under N_2 for 4 h. The brown solution was then cooled to room temperature and sealed under N_2. After 6 d the yellow product precipitated. The solid was washed with hexane and dried *in vacuo*. Yield: 0.07 g (43%). Complex (**2**) was soluble in all common organic solvents except hexane (Found: C, 24.60; H, 1.05; F, 22.95. Calc. for $C_{15}H_{11}F_9Mo_2O_{12}$: C, 24.15; H, 1.50; F, 22.90%).

$[Ru_2(\mu\text{-asp})_4Cl]$ (**3**).—*Method* 1. The complex $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ (0.30 g, 0.63 mmol), Hasp (0.91 g, 5.1 mmol), and methanol (20 cm^3) were refluxed under N_2 for 12 h. The resulting red-brown solution was rotary evaporated (at *ca.*

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* We have recently synthesized a nitroso/benzoate/methoxide complex using a method similar to that used to prepare (**7**).

30 °C) to low volume and the red-brown product precipitated. The solid was washed with small volumes of methanol and then air-dried. Yield: 0.42 g (70%).

Method 2. The complex $[Ru_2(\mu\text{-}O_2CC_6H_5)_4Cl]$ (0.23 g, 0.32 mmol), Hasp (0.96 g, 5.3 mmol), and methanol (30 cm^3) were refluxed under N_2 for 24 h. The resulting red-brown solution was treated as in Method 1. Complex (**3**) was soluble in methanol, ethanol, acetonitrile, and tetrahydrofuran, and was insoluble in chloroform, diethyl ether, acetone, and water (Found: C, 45.35; H, 3.00; Cl, 3.55. Calc. for $C_{36}H_{28}ClO_{16}Ru_2$: C, 45.30; H, 2.95; Cl, 3.70%). $\Lambda_M = 7$ S cm^2 mol^{-1}, $\mu_{eff.} = 3.7$ per Ru_2.

$[Ru_2(\mu\text{-asp})_2(\mu\text{-}O_2CC_6H_5)_2Cl]\cdot H_2O$ (**4**).—Complex (**3**) (0.34 g, 0.35 mmol), benzoic acid (0.09 g, 0.74 mmol), and methanol (40 cm^3) were refluxed under N_2 for 12 h. The solution was then cooled to room temperature and stirred under N_2 for a further 72 h. The resulting orange solution was rotary evaporated to *ca.* 5 cm^3 and the orange product precipitated. The solid was washed with methanol and then air-dried. Complex (**4**) was soluble in hot methanol and ethanol, and was insoluble in water and chloroform (Found: C, 44.60; H, 3.05; Cl, 4.05. Calc. for $C_{32}H_{26}ClO_{13}Ru_2$: C, 44.90; H, 3.05; Cl, 4.15%). $\Lambda_M = 62$ S cm^2 mol^{-1}, $\mu_{eff.} = 4.2$ per Ru_2.

$[Ru_2(\mu\text{-asp})_4(O_2CCF_3)]\cdot 2H_2O$ (**5**).—Complex (**3**) (0.40 g, 0.42 mmol), $Ag(O_2CCF_3)$ (0.10 g, 0.45 mmol), and methanol (40 cm^3) were refluxed under N_2 for 12 h. Silver chloride (0.06 g, 0.42 mmol) was filtered off and the orange filtrate was rotary evaporated to *ca.* 6 cm^3. The product precipitated as an orange solid. The solid was washed with ether and then air-dried. Complex (**5**) was soluble in methanol and ethanol (Found: C, 42.50; H, 2.80; F, 4.85. Calc. for $C_{38}H_{32}F_3O_{20}Ru_2$: C, 42.75; H, 3.00; F, 5.35%). $\Lambda_M = 67$ S cm^2 mol^{-1}, $\mu_{eff.} = 4.3$ per Ru_2.

$[Ru_2(\mu\text{-asp})_4(NO_3)]\cdot H_2O$ (**6**).—To a solution of complex (**3**) (0.33 g, 0.35 mmol) in methanol (25 cm^3) was added an aqueous solution of silver nitrate (0.06 g, 0.34 mmol $AgNO_3$ in 3 cm^3 of water) and the mixture stirred for 5 min at *ca.* 20 °C. Silver chloride (0.05 g, 0.34 mmol) was filtered off and the orange filtrate was rotary evaporated (at *ca.* 30 °C) to *ca.* 8 cm^3. The product precipitated as orange microcrystals. The solid was washed with small portions of water–methanol (80:20), and dried *in vacuo.* Yield: 0.24 g (67%). Complex (**6**) was soluble in methanol, ethanol, and acetone, and was insoluble in water (Found: C, 43.65; H, 3.25; N, 1.35. Calc. for $C_{36}H_{30}NO_{20}Ru_2$: C, 43.30; H, 3.05; N, 1.40%). $\Lambda_M = 60$ S cm^2 mol^{-1}, $\mu_{eff.} = 3.9$ per Ru_2.

$[Ru_2(\mu\text{-asp})_4(NO)]\cdot 4H_2O$ (**7**).—Quantities of complex (**3**), methanol, and aqueous silver nitrate were as specified for the preparation of (**6**). The reactants were refluxed (*ca.* 70 °C) under N_2 for 4 h and the solution changed colour from red to brown. Silver chloride (0.05 g, 0.34 mmol) was filtered off and the filtrate was rotary evaporated to *ca.* 4 cm^3. The product precipitated as a dark brown solid. The solid was washed with small portions of water and then dried *in vacuo.* Yield: 0.27 g (76%). Complex (**7**) was soluble in methanol and ethanol, and was insoluble in dichloromethane and water. Note: complex (**7**) was recovered when (**6**) was either (*i*) refluxed in methanol for 3 h, or (*ii*) allowed to stand in methanol (20 °C) for a period of 3—4 weeks (Found: C, 41.95; H, 3.45; N, 1.10. Calc. for $C_{36}H_{36}NO_{21}Ru_2$: C, 42.35; H, 3.55; N, 1.35%). $\Lambda_M = 19$ S cm^2 mol^{-1}, $\mu_{eff.} = 3.1$ per Ru_2.

Reaction of $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ *with Nitric Acid.*—A sample of $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ (0.05 g) was dissolved in a small volume of concentrated nitric acid at *ca.* 20 °C to give a purple solution. After standing in air for *ca.* 2 weeks a dark purple solid (**8**) precipitated. When the remaining purple filtrate was rotary evaporated (at *ca.* 100 °C) it changed to a dark brown colour, and on taking to dryness a brown tar (**9**) formed.

Reaction of '$RuCl_3\cdot 3H_2O$' *with Nitric Acid.*—A mixture of '$RuCl_3\cdot 3H_2O$' (0.05 g) and silver nitrate (0.017 g) in concentrated nitric acid was stirred at *ca.* 20 °C for 12 h. Silver chloride was removed by filtration. The brown filtrate was then evaporated to dryness (*ca.* 100 °C), leaving a brown residue (**10**).

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