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Terminal water ligand exchange and substitution by isonicotinamide on the oxo-centred triruthenium(III) complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$. Crystal structure of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4\cdot HClO_4\cdot H_2O$

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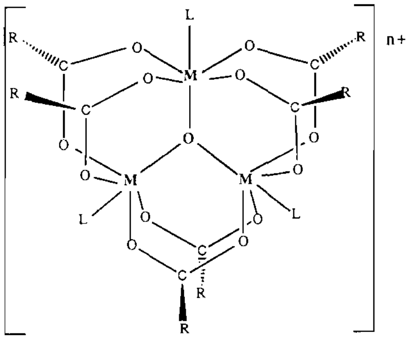
Abstract

A study or water exchange and substitution by isonicotinamide on the triruthenium carboxylate complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ using ^{17}O NMR and UV–Vis spectrophotometry has been carried out in aqueous perchlorate media, $I = 1.0$ M. The present results represent the first such kinetic studies carried out on this complex in aqueous media and provide support for a general I_d mechanism for substitution/exchange reactions at the terminal L ligands in $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6L_3]^+$ complexes. The X-ray crystal structure reported for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4\cdot HClo_4\cdot H_2O$ is the first such structure on a triruthenium(III) carboxylate complex and provides evidence of a significant elongation in the Ru–O(OH_2) bond length (av. 2.091 Å) when compared to that, for example, in $[Ru(OH_2)_6]^{3+}$ (2.029 Å). It is concluded that a significant *trans* labilisation effect from the planar μ_3-oxo ligand is relevant for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ and responsible for a water exchange rate constant (25 °C) some $10^3\times$ larger than that on the hexaaqua ion.

Introduction

Trinuclear planar oxo-centred basic carboxylates [1] $[M_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6L_3]^{n+}$ are now known for a diverse range of trivalent metals (Ti [2], V [3], Cr [4], Mn [5], Fe [6], Co [7], Ru [8, 9], Rh [10, 11], Ir [12] and Ga [13]), R groups and terminal L ligands (H_2O, pyridine, isonicotinamide, CH_3OH, THF, DMF and PPh_3). The trinuclear formulation was first proposed in 1908 by Weinland [14] and Werner [15] for the basis acetate of Cr(III) ($R = CH_3$, $L = H_2O$). However it was not until 1965 that X-ray crystallography [4] established the planar μ_3-O triangular structure (I) of the Cr compound thus confirming the subsequent predictions of Welo [16] in 1928 and of Orgel [17] in 1960.

Interest in these compounds has arisen for several reasons. Firstly they form a rare class of compound known for earlier, middle and late as well as first, second and third row transition elements upon which to conduct comparative studies. Secondly the polynuclear structure lends itself to the formation of mixed-valence and mixed-metal derivatives allowing an opportunity to study electronic and magnetic interactions between homo and heterometal centres in close proximity in a defined geometry. There is also the possibility of generating spin-frustrated species. Thirdly several of the complexes are active as homogeneous catalysts for a variety of oxidation reactions including air oxy-



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genation of cyclic aliphatic [18, 19] and aromatic [7] hydrocarbons (M = Fe, Ru, Co, Mn), oxidation of alcohols [20] (M = Ru) and epoxidation [21] (M = Fe), hydrogenation [22] (M = Ru) and isomerisation [22] (M = Ru) or olefins amongst others [23]. In view of this, most attention has tended to focus on the electronic, magnetic and redox properties of these complexes [1]. Surprisingly little attention has been paid to a consideration of substitution properties with few reports of detailed kinetic studies regarding complexation of the L ligands, especially for L = H_2O. There is interest in establishing how the carboxylato trinuclear structure affects the lability of the terminal ligands versus that of simple mononuclear complexes of the same metal. In water, however, such studies on many of the carboxylate complexes of the first row metals are limited owing to the need to have a large excess of free carboxylate ions present in solution in order to stabilise the complexes. On the other hand, the complexes formed by the second and third row metals are much more stable and, for M = Ru, L = pyridine [9] or isonicotinamide [24], further interest stems from the availability of a range of oxidation states viz. $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6L_3]^{n+}$ ($n = 2, 1, 0, -1, -2$). Sasaki *et al.* have recently reported a ^1H NMR kinetic study of the CD_3OD substitution for terminal H_2O on the Ru(III,III,III) aqua complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ conducted in pure CD_3OD [25]. However no corresponding substitution studies appear to have been carried out solely in aqueous media. We wish to report herein the results of kinetic studies of water exchange (using ^{17}O NMR) and substitution of terminal water by iso (using visible spectrophotometry) carried out on $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ in aqueous perchlorate media. In addition we report the first X-ray crystal structure of a complex containing the $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ unit. With these results it is now possible to assess the intrinsic lability of the water ligands in this complex and assign the mechanism of substitution.

Experimental

Preparation of μ_3-oxohexakis(μ-acetato)-triaqua-triruthenium(III) perchlorate, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4$

The green acetato salt $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]O_2CCH_3$ was first prepared from $RuCl_3 \cdot nH_2O$ (Johnson Matthey) according to the method of Wilkinson and co-workers [26] and its purity confirmed by its electronic spectrum in methanol, $\lambda_{max} = 686$ nm ($\epsilon = 1100$ M^{-1} cm^{-1} per Ru_3) [8]. The perchlorate salt was then prepared from the acetate salt using cation-exchange chromatography [27]. A sample of the acetate salt (~1.0 g) was dissolved in water and adjusted to pH 2.5 with dilute $HClO_4$ to ensure it was present in the fully protonated 1+ form. The green solution was then loaded onto a column of Dowex 50W X2 cation-exchange resin (H^+ form) (10×2 cm) wherein a pale greenish solution emerged from the column while a deep blue band was retained. The column was washed with 0.01 M $HClO_4$ and the blue band subsequently eluted with 1.0 M $HClO_4$. Slow evaporation of the eluate in a dessicator over silica gel gave rise to dark purple–blue lustrous crystals of the perchlorate salt [28]. The presence of the $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ unit was confirmed by UV–Vis spectrophotometry, in both the solid state and in 0.1 M $HClO_4$ solution ($\lambda_{max} = 686$ nm, $\epsilon = 1100$ M^{-1} cm^{-1} per Ru_3) [8] and by microanalysis. *Anal.* found: C, 15.20; H, 2.78. Calc. for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4 \cdot HClO_4 \cdot H_2O$ ($C_{12}H_{27}O_{25}Ru_3Cl_2$): C, 15.24; H, 2.88%. The presence of one $HClO_4$ molecule was also confirmed in the crystal structure.

Preparation of μ_3-oxohexakis(μ-acetato)-tris(isonicotinamide)triruthenium(III) hexafluorophosphate, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(iso)_3]PF_6$ [24]

The acetate salt (0.04 g) was dissolved in the minimum volume of water and an excess of isonicotinamide (0.03 g) was added. The solution was heated for ~10 min and then allowed to cool. During the cooling process solid NH_4PF_6 was added until the solution became cloudy. Following filtration and further cooling blue microcrystals of the title complex separated and were collected by filtration, washed with diethyl ether and dried (dessicator over silica gel). Its visible spectrum in methanol ($\lambda_{max} = 700$ nm, $\epsilon = 6300$ M^{-1} cm^{-1}) was in close agreement with the literature value [24].

Crystal structure of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4 \cdot HClO_4 \cdot H_2O$

A suitable crystal for X-ray investigation was obtained by slow evaporation of solutions of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ in 1.0 M $HClO_4$. X-ray data were recorded on a crystal of dimensions 0.29×0.31×0.45 mm, sealed in a thin walled capillary, using graphite monochromated Mo Kα radiation from a Siemens R3m/v diffractometer, ω scan mode with variable scan speed 1.50 to 14.65 °/min in ω.

Crystal data

$C_{12}Cl_2H_{27}O_{25}Ru_3$, $M_r = 945.42$, monoclinic, space group $P2_1/n$, $a = 11.121(3)$; $b = 15.480(13)$; $c = 17.190(21)$ Å, $\beta = 91.72(10)°$, $U = 2959$ Å^3 (by least-squares refinement on diffractometer angles for 20 reflections in the range $15 < 2\theta < 28°$ (Mo Kα, $\lambda = 0.71073$ Å)). A total of 3056 reflections was measured with $2.0 < 2\theta < 50°$, $+h$, $+k$, $+l$, 2019 observed with $F_o > 6.0\sigma(F_o)$. No significant crystal decay was found. Lorentz and polarisation corrections were applied to the data as well as an empirical absorption correction [29].

Structure analysis and refinement

The structure was solved using a Patterson synthesis to locate the Ru atoms (SHELXTL). Other non-H atoms were located after successive Fourier syntheses and least-squares refinement. The H atoms were placed in calculated positions on the cation using a riding model. The Cl and O atoms of the perchlorate/perchloric acid molecules could be located easily but it was not possible to suggest which of these might be the perchloric acid of crystallisation. One water of crystallisation per asymmetric unit was located. There is evidence from the residual electron density (+3.13 and −1.92 e Å^{-3} in the final difference map) that there may be more lattice water disordered throughout the crystal. The crystals themselves show some evidence of non-crystallinity and possibly twinning in that the reflection profiles are not smooth. It is not possible to say whether this is because of long range lattice disorder or a twinning problem. However the overall crystal structure of the $\{Ru_3O\}^{7+}$ moieties and the ClO_4^- groups can be deduced from the diffraction data obtained yielding R values of 11.82% and weighted $R = 13.36\%$ (weight $= 1/[\sigma^2(F_o) + 0.01485F_o^2]$). In view of the quality of data obtained only the Ru atoms were refined anisotropically. The final data/parameter ratio was 11.0:1. Fractional atomic coordinates and equivalent isotropic displacement coefficients are given in Table 1. See also 'Supplementary material'.

Other reagents

Manganese(II) perchlorate hexahydrate, sodium perchlorate, sodium acetate and perchloric acid (all Aldrich AR grade) were used as supplied. All other reagents and solvents used were of reagent grade quality and used as supplied. Solutions of sodium perchlorate were standardised by exchange onto columns of Amberlite IR(H)120 resin (H^+ form, BDH analar) and the H^+ released titrated with standard NaOH. Double distilled water was used throughout.

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]ClO_4 \cdot HClO_4 \cdot H_2O$

	x	y	z	U_{eq}[a]
Ru(1)	1667(3)	2920(1)	5900(1)	20(1)
Ru(2)	1559(3)	2051(1)	4148(1)	22(2)
Ru(3)	4177(4)	2527(2)	4989(1)	22(2)
O(1)	2560(36)	2516(11)	5020(9)	19(4)
O(2)	430(24)	3620(12)	5266(9)	26(5)
O(3)	402(28)	3030(15)	4109(12)	46(6)
C(1)	53(37)	3588(18)	4595(14)	26(7)
C(2)	−825(40)	4198(21)	4338(16)	40(8)
O(4)	485(29)	1947(15)	5948(12)	47(6)
O(5)	452(25)	1328(12)	4804(10)	28(5)
C(3)	131(36)	1410(17)	5453(14)	23(6)
C(4)	−803(42)	736(23)	5709(18)	48(9)
O(6)	2771(29)	2332(13)	6669(10)	34(5)
O(7)	4412(31)	2083(17)	6074(14)	57(7)
C(5)	3774(47)	2037(21)	6612(17)	37(8)
C(6)	4342(38)	1628(22)	7366(16)	40(8)
O(8)	2690(29)	4018(15)	5979(12)	45(6)
O(9)	4371(28)	3748(15)	5407(12)	44(6)
C(7)	3594(47)	4257(24)	5749(19)	49(9)
C(8)	4158(41)	5134(22)	5960(17)	45(9)
O(10)	4298(31)	1325(17)	4570(14)	59(7)
O(11)	2654(32)	1010(15)	4004(12)	45(6)
C(9)	3555(48)	845(22)	4248(18)	39(8)
C(10)	4085(47)	−57(25)	4032(20)	64(12)
C(12)	4244(28)	3013(14)	3905(12)	39(6)
O(13)	2431(30)	2708(14)	3349(11)	39(6)
C(11)	3446(47)	3026(21)	3387(17)	37(8)
C(12)	3895(42)	3516(23)	2635(17)	48(10)
O(14)	755(24)	3388(13)	6887(10)	34(5)
O(15)	506(24)	1546(12)	3194(10)	30(5)
O(16)	5982(38)	2519(16)	4978(12)	59(8)
Cl(1)	7619(15)	4166(8)	6482(7)	75(3)
O(17)	6557(36)	4314(23)	6983(17)	97(11)
O(18)	7538(50)	4938(34)	6040(28)	180(19)
O(19)	8660(62)	3994(38)	6965(32)	185(23)
O(20)	7476(49)	3436(34)	6091(27)	156(18)
Cl(2)	2242(17)	−294(10)	6658(7)	95(4)
O(21)	2481(35)	191(22)	5958(17)	102(10)
O(22)	3476(35)	−526(22)	7084(17)	93(10)
O(23)	1753(54)	−1015(33)	6395(26)	153(19)
O(24)	1406(50)	184(34)	7193(26)	162(18)
O(25)	−2921(42)	2585(24)	3562(20)	112(13)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Instrumentation

UV–Vis spectra and fixed wavelength kinetics were recorded in 1 cm quartz cuvettes using a Perkin-Elmer Lambda 5 spectrophotometer with electronic thermostatting and auto cell change facilities. A Radiometer PHM82 pH meter was used with a Russell CWR/320/757 narrow stem combination glass/Ag/AgCl electrode which allowed direct pH measurement inside the 1 cm cuvettes. The pH meter was calibrated with solutions at pH 2 and pH 4 at $I = 1.0$ M ($NaClO_4$).

Kinetics of complex formation by isonicotinamide

This was followed at three temperatures 40, 45 and 50 °C using an excess of isonicotinamide (0.1–0.5 M) over complex ($\sim 3.7 \times 10^{-4}$ M) in the pH range 2.4–3.5 at $I = 1.0$ M ($NaClO_4$). In each case the pH values were adjusted with the required amounts of $HClO_4$ or NaOH and the solutions (~ 3.0 cm^3) equilibrated for ~15 min inside the spectrophotometer before absorbance–time readings were commenced. In all cases there was close agreement between initial and final pH values (within 0.05 pH unit). Data was collected over 30 min time intervals at 360 nm. First order rate constants (k_{obs} (s^{-1})) were obtained from the slopes of $\ln(A_{inf}-A_t)$ versus t plots by a standard least-squares treatment. In all cases plots were linear to greater than 3 half-lives.

Kinetics of water exchange

This was carried out at 25 °C by mixing natural abundance solutions of the perchlorate salt with amounts of 10 at.% ^{17}O enriched water (Yeda, Israel) to a final volume of 2.0 cm^3 containing 0.02 M in complex, H^+ 0.60 M and $I=1.0$ M ($NaClO_4$). The final enrichment was ~6 at.%. ^{17}O NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 40.56 MHz. Manganese(II) perchlorate was added prior to mixing with enriched water in order to remove the intense ^{17}O resonance link of bulk water by paramagnetic exchange broadening [30]. Solutions were equilibrated for about 5 min before accumulations were commenced. Spectra were recorded over a total sweep range of 62 500 Hz using 10 000 transients over time intervals of 104 s. The 90° pulse width was 27 μs. Rate constants were obtained by fitting the growth in the height of the ^{17}O resonance line of bound water to the exponential function ($(1-\exp(-kt)+\text{offset})$ using a non-linear least-squares Marquardt treatment. The resonance of non-exchanging ClO_4^- ion (+288 ppm from bulk water) served as a useful internal reference line. The peak heights recorded were thus the ratio of the height of the bound water resonance to that of ClO_4^-.

Results and discussion

Structure of [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3$]-$ClO_4 \cdot HClO_4 \cdot H_2O$

The structure of the triaqua perchlorate salt is characterised by both $HClO_4$ and H_2O molecules of crystallisation. This almost certainly stems from the crystallisation method involving slow evaporation from solutions in 1.0 M $HClO_4$. The crystal packing diagram, Fig. 1, shows an extensive network of hydrogen bonds (dotted lines) occurring between coordinated water molecules and the ClO_4^- ions. Selected bond lengths and angles are listed in Table 2. Although the three Ru atoms define an almost perfect equilateral triangle (each Ru–Ru–Ru angle = 60 (± 0.1)°), Fig. 2, the central planar μ_3-O group is displaced from the centre of gravity of this triangle, being nearer to Ru(3) and equidistant from the other two Ru atoms. The consequence of this is a significant distortion from trigonal geometry at this oxygen. The three Ru–(μ_3-O)–Ru angles are respectively 114.8, 121.4 and 123.8°, Table 2. In addition the Ru–O(OH_2) distance appears to be shorter for Ru(3) than for the other Ru atom. Consequently, the system can be regarded as possessing a plane of symmetry through O(1)–Ru(3)–O(16). The average Ru–Ru distance (3.298 Å) is similar to the M–M separation in a range of μ_3-oxo trinuclear carboxylato trivalent metal complexes, Table 3, and thus rules out the presence of a direct Ru–Ru bond. The present structure is the first on a triruthenium(III) aqua carboxylate complex. In view of the presence of two ClO_4^- ions and apparent distortion from three-

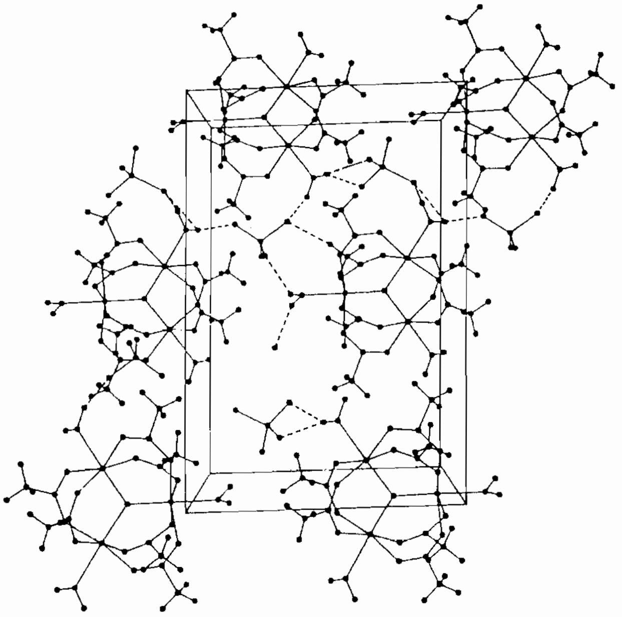

Fig. 1. Diagram of the crystal packing in the [$Ru_3O(CH_3CO_2)_6(OH_2)_3$]$^+$ cation. The hydrogen bonds are represented by dotted lines.

TABLE 2. Selected bond lengths (Å) and angles (°) for [$Ru_3(\mu_3$-$O)(\mu CH_3CO_2)_6(OH_2)_3$]$ClO_4 \cdot HClO_4 \cdot H_2O$ showing the coordination environment of the Ru atoms

Bond lengths (Å)			
Ru(1)–Ru(2)	3.299(5)	Ru(1)–Ru(3)	3.299(6)
Ru(1)–O(1)	1.939(25)	Ru(1)–O(2)	2.041(22)
Ru(1)–O(4)	2.004(28)	Ru(1)–O(6)	1.998(25)
Ru(1)–O(8)	2.046(26)	Ru(1)–O(14)	2.130(21)
Ru(2)–Ru(3)	3.295(6)	Ru(2)–O(1)	1.976(25)
Ru(2)–O(3)	1.988(27)	Ru(2)–O(5)	2.032(22)
Ru(2)–O(11)	2.040(28)	Ru(2)–O(13)	1.985(24)
Ru(2)–O(15)	2.134(20)	Ru(3)–O(1)	1.801(40)
Ru(3)–O(7)	1.998(24)	Ru(3)–O(9)	2.032(23)
Ru(3)–O(10)	2.000(26)	Ru(3)–O(12)	2.012(20)
Ru(3)–O(16)	2.008(43)	O(2)–C(1)	1.216(32)
Bond angles (°)			
Ru(2)–Ru(1)–Ru(3)	59.9(1)	Ru(1)–O(1)–Ru(2)	114.8(20)
Ru(1)–Ru(2)–Ru(3)	60.0(1)	Ru(2)–O(1)–Ru(3)	121.4(12)
Ru(1)–Ru(3)–Ru(2)	60.0(1)	Ru(1)–O(1)–Ru(3)	123.8(13)

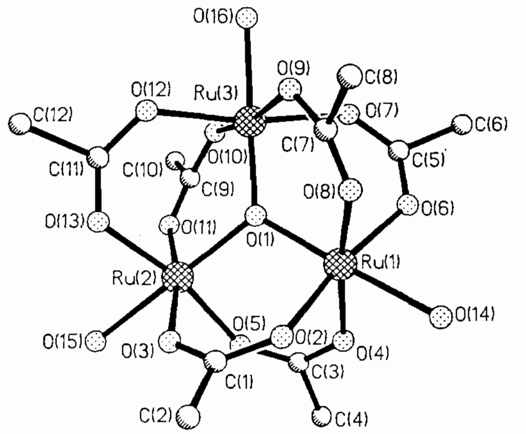

Fig. 2. View of the trinuclear unit of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ showing the numbering scheme.

fold symmetry, the possibility of the crystalline complex actually consisting of a mixed-valence species with one Ru(IV) centre (Ru(3)) was considered. This was quickly ruled out on the basis of the solid state visible spectrum of the powdered crystals which matched that of the solution spectrum of the crystals dissolved in 0.1 M $HClO_4$ verifying the presence of the $\{Ru^{III}_3O\}$ unit. $\{Ru^{III,III,IV}_3O\}$ units have markedly different electronic spectral features [24]. It was thus concluded that one $HClO_4$ molecule of crystallisation was present. The equivalence of the two ClO_4^- ions suggests that the proton is free and presumably associated with the extensive hydrogen-bonded network and possibly extra lattice water. Finally, because of the large R value (12–13%) in the structure, we feel that it may be premature to attach a chemical significance to the shorter Ru–O(16)(OH_2) distance in terms of solution properties (i.e. enhanced acidity and/or more inert behaviour of the bound water). For the purpose of a comparison of Ru–OH_2 bond lengths and in discussing the kinetics of isonicotinamide complexation and water exchange, we have assumed chemical equivalence of the three Ru centres.

Kinetics of complex formation by isonicotinamide

Figure 3 shows typical UV–Vis spectral changes in the $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ complex (3.7×10^{-4} M) obtained at pH 3.2 over 30 min time intervals at 50 °C following addition of an excess of isonicotinamide (0.3 M), $I = 1.0$ M ($NaClO_4$). The reaction proceeds with a gradual increase in absorbance in the range 300–850 nm and a shift in λ_{max} from 686 nm (triaqua complex) towards 700 nm (substitution by isonicotinamide). Plots of k_{obs} versus total concentration of isonicotinamide $[iso]_T$, Fig. 4, consisted of straight lines passing through the origin indicating that no appreciable aquation (back) reaction was involved in the rate determining step. The absence of curvature in plots for up to 0.5 M in $[iso]_T$ indicated that ion pairing was not significant.

Dependence upon hydrogen ion concentration

The acid dissociation constant, K_{iso}, at 25 °C is 2.4×10^{-4} M (pK_{iso} 3.67) [31] indicating that appreciable amounts of the protonated ligand, Hiso, are present in the pH range of study, (2.4–3.5). Thus $[iso]_T$ can be represented by eqn. (1).

$$[iso]_T = [Hiso] + [iso] \qquad (1)$$

In addition, the water ligands of the triaquatriruthenium complex are weakly acidic ($K_a^1K_a^2 = 4.47 \times 10^{-5}$ M^2) for the first two deprotonations [8]. The pK_a value for loss of a third proton is estimated to be >12 [8]. Spencer and Wilkinson reported that K_a^1 and K_a^2 were not resolvable, meaning that one could consider only the triaqua and aquadihydroxy forms of the complex as being relevant to the pH range of the present study. Thus the total Ru_3 concentration $[Ru_3]_T$ may be represented by eqn. (2).

$$[Ru_3]_T = [Ru_3O(CH_3CO_2)_6(OH_2)_3{}^+] + [Ru_3O(CH_3CO_2)_6(OH)_2(OH_2)^-] \qquad (2)$$

The pH was thus varied in order to establish which species are involved in the rate determining process. The slopes of k_{obs} versus $[iso]_T$ plots, Fig. 4, increase with decreasing $[H^+]$. It it is assumed that the protonated form of iso will be unable to take part in the complexation reaction then one can consider the two forms of the

TABLE 3. Structural data for various trimetal carboxylate complexes

Compound	Space group	M–(μ_3-O) (Å)	M–O[a] (Å)	M–M (Å)	Ref.
$[Cr_3O(CH_3CO_2)_6(OH_2)_3]Cl \cdot H_2O$	$P2_12_12$	1.89	1.97	3.28	4b
$[Fe_3O(CH_3CO_2)_6(OH_2)_3]ClO_4$	$P2_1/c$	1.91	2.02	3.29	6
$[V_3O(CH_2ClCO_2)_6(OH_2)_3]ClO_4$	$P2_1/c$	1.93	2.01	3.34	3a
$[Rh_3O(CH_3CO_2)_6(OH_2)_3]ClO_4 \cdot 2H_2O$	$P2_1/c$	1.92	2.01	3.33	11
$[Ru_3O(CH_3CO_2)_6(OH_2)_3]ClO_4 \cdot HClO_4 \cdot H_2O$	$P2_1/n$	1.91	2.02	3.30	this work

[a] For M–O (carboxylate).

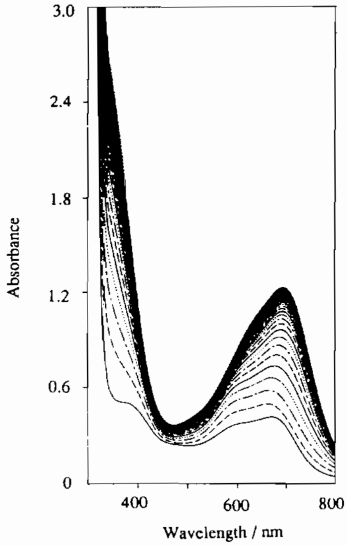

Fig. 3. UV-Vis spectral changes obtained at 30 min intervals following mixing of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ (3.7×10^{-4} M) and isonicotinamide (0.30 M) at 50 °C, pH 3.2, $I=1.0$ M ($NaClO_4$).

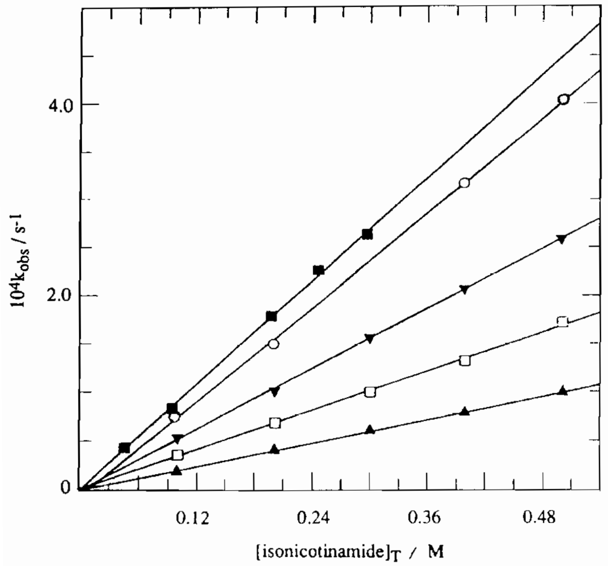

Fig. 4. Dependence of first order rate constants, k_{obs} (s^{-1}) (50 °C), on $[isonicotinamide]_T$ for reaction with $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ at different pHs, $I=1.0$ M ($NaClO_4$). (■) pH 3.44, (○) 3.30, (▼) 3.06, (□) 2.77 and (▲) 2.45.

Ru_3 complex reacting solely with iso according to eqns. (3)–(7)

$$[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+ \xrightleftharpoons{K_a{}^1} [Ru_3O(CH_3CO_2)_6(OH_2)_2(OH)]+H^+ \quad (3)$$

$$[Ru_2O(CH_3CO_2)_6(OH_2)_2(OH)] \xrightleftharpoons{K_a{}^2} [Ru_3O(CH_3CO_2)_6(OH_2)(OH)_2]^- +H^+ \quad (4)$$

$$Hiso \xrightleftharpoons{K_{iso}} iso+H^+ \quad (5)$$

$$[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+ + iso \xrightarrow{k_1} products \quad (6)$$

$$[Ru_3O(CH_3CO_2)_6(OH_2)(OH)_2]^- + iso \xrightarrow{k_2} products \quad (7)$$

from which, abbreviating triaqua and aquadihydroxy complexes to Ru_3 and $Ru_3(OH)_2$, the overall rate may be expressed as eqn. (8). Since the triaqua complex has three equivalent Ru centres

$$Rate=(k_1/3)[Ru_3][iso]+k_2[Ru_3(OH)_2][iso] \quad (8)$$

a statistical factor has been assumed relevant to k_1 [32]. From a consideration of expressions relating [iso], $[Ru_3]$ and $[Ru_3(OH)_2]$ to $[iso]_T$ and $[Ru_3]_T$, respectively, it is possible to derive eqn. (9) for the pseudo first order rate constant, k_{obs}.

$$k_{obs}=\frac{((k_1/3)K_{iso}[H^+]^2+k_2K_a{}^1K_a{}^2K_{iso})[iso]_T}{([H^+]^2+K_a{}^1K_a{}^2)(H^+]+K_{iso})} \quad (9)$$

Consistent with eqn. (9) subsequent plots of $k_{obs}(H^+]^2+K_a{}^1K_a{}^2)([H^+]+K_{iso})/[iso]_T$ versus $[H^+]^2$ are linear and the data for three temperatures are illustrated in Fig. 5. Values of k_1 and k_2 at each of the three temperatures along with their associated activation parameters are listed in Table 4.

Product analysis

The UV-Vis spectra at infinity showed a maximum at 700 nm ($\epsilon=3230$ M^{-1} cm^{-1} per Ru_3) which may

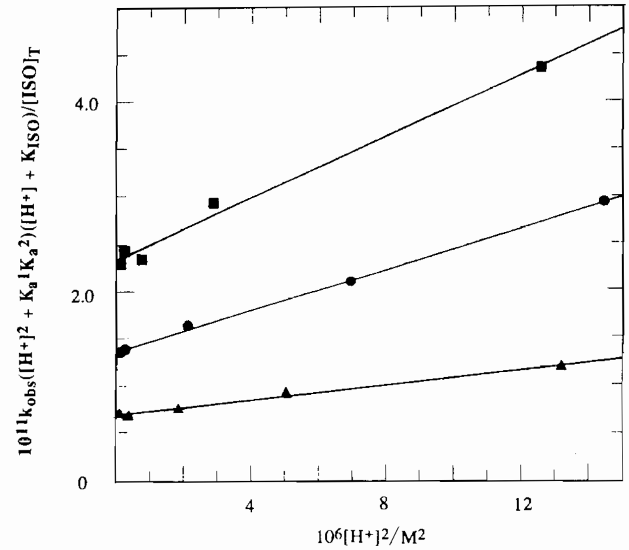

Fig. 5. Plots of k_{obs} $([H^+]^2+K_a{}^1K_a{}^2)([H^+]+K_{iso})/[iso)_T$ vs. $[H^+]^2$ for reaction of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ with isonicotinamide at three temperatures, $I=1.0$ M ($NaClO_4$). (▲) 40 °C, (●) 45 °C and (■) 50 ° C.

TABLE 4. Values of k_1 (M^{-1} s^{-1}) and k_2 (M^{-1} s^{-1}) in eqn. (9) as a function of temperature and corresponding activation parameters representing the reaction of isonicotinamide with $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^+$ and $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH)_2(OH_2)]^-$, $I = 1.0$ M ($NaClO_4$)

Temp. (°C)	$10^3 \times k_1$ (M^{-1} s^{-1})	$10^3 \times k_2$ (M^{-1} s^{-1})
40.0	5.47	0.71
45.0	12.66	1.44
50.0	22.66	2.44

$\Delta H_1^{*} = 116.9 \pm 11.4$ kJ mol^{-1}; $\Delta H_2^{*} = 101.2 \pm 7.8$ kJ mol^{-1}
$\Delta S_1^{*} = 85.1 \pm 36.0$ J K^{-1} mol^{-1}; $\Delta S_2^{*} = 17.8 \pm 24.6$ J K^{-1} mol^{-1}

be compared to that from a solution of the tris(isonicotinamide) complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(iso)_3]^+$ ($\lambda_{max} = 700$ nm ($\epsilon = 6300$ M^{-1} cm^{-1}) [24]. If the run solutions at infinity were allowed to stand at room temperature for 1–2 days a blue feathery solid was precipitated which was found to be contaminated with excess isonicotinamide. This proved difficult to remove. However a fast atom bombardment mass spectrum recorded on the isolated solid showed an intense *m/e* peak at 1041 for $[^{102}Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(iso)_3]^+$ and a characteristic fragmentation pattern showing successive loss of three isonicotinamide molecules. In the absence of reliable analytical data two explanations for the results are possible. Firstly the final product, despite the absence of equilibration kinetics, is a mixture of isonicotinamide substituted products 1:1, 1:2 and 1:3 (low ϵ value at 700 nm) with the trisubstituted product the least soluble and precipitated after 1–2 days. Alternatively, the mixture of products could have been precipitated but the FAB mass spectrum only shows evidence of the trisubstituted product.

Kinetics of water exchange

Figure 6 shows the increase in height (arbitrary units) of the ^{17}O NMR resonance of bound water on $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ as a function of time at 25 °C from which the rate constant for water exchange was determined to be $(1.08 \pm 0.07) \times 10^{-3}$ s^{-1}. For some runs there was a delay in the onset of water exchange which correlated with the appearance of a transient purple colour in the perchloric acid solutions prior to generation of the normal turquoise colour of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ [8]. This was eventually traced to the use of concentrated 70% $HClO_4$ as the source of $[H^+]$ in making up the solutions for exchange. Solutions (> 6.0 M) in $HClO_4$ cause spontaneous rapid oxidation to the purple Ru(III,III,IV) dicationic complex (λ_{max} at 314, 560 and 760 nm) [24] which upon dilution of the $[H^+]$ results in slow autoreduction to Ru(III,III,III) (λ_{max} at 686 nm). Water exchange on the Ru(III,III,IV) complex appears to be several orders of magnitude slower than on the Ru(III,III,III) form and is responsible for the delay in the onset of water exchange in the latter. The greater inertness of the water ligands of the Ru(III,III,IV) complex probably stems from the higher cationic charge (2+).

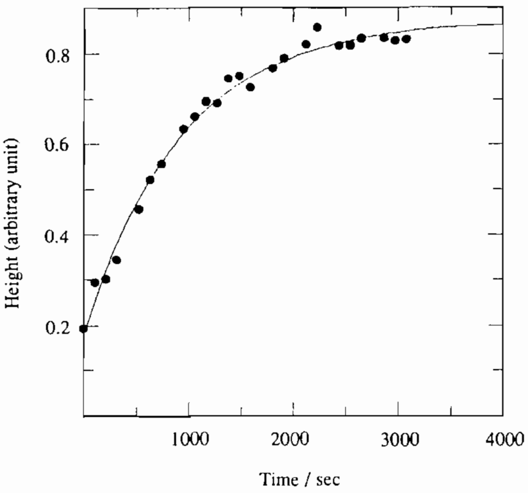

Fig. 6. Increase in relative height of the ^{17}O NMR resonance of bound water on $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ as a function of time, 25 °C, $[H^+] = 0.60$ M, $I = 1.0$ M ($NaClO_4$). The line drawn through the points is a standard least-squares fitted exponential function.

One can now attempt to compare the rate constant for water exchange on $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ at 25 °C with those for complex formation by isonicotinamide and CD_3OD. Bearing in mind one is comparing first and second order rate constants, the statistically corrected k_1 value (25 °C) for complexation by isonicotinamide (0.57×10^{-3} M^{-1} s^{-1}) is of the same magnitude as the value for water exchange (1.08×10^{-3} s^{-1}) and 1:1 complexation by CD_3OD (0.56×10^{-3} s^{-1}, 21 °C) [25]. Activation parameters are also similar for both incoming ligands, $\Delta H^{\ddagger} = 117$ kJ mol^{-1}, $\Delta S^{\ddagger} = +85$ J K^{-1} mol^{-1} (isonicotinamide); $\Delta H^{\ddagger} = 103$ kJ mol^{-1}, $\Delta S^{\ddagger} = +41$ J K^{-1} mol^{-1} (CD_3OD) [25%. On the other hand for $[Ru_3O(CH_3CO_2)_6py_3]^+$, rate constants for terminal pyridine exchange are much smaller ($k_{py} = 2.2 \times 10^{-4}$ s^{-1}, 70 °C) [33] suggestive of a significant leaving ligand effect. Taken together the evidence suggests a dissociative I_d mechanism for terminal ligand L substitution on $[Ru_3O(CH_3CO_2)_6L_3]^+$.

The rate constant for water exchange on $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ (25 °C) is some three orders of magnitude larger than that for $[Ru(OH_2)_6]^{3+}$ (3.5×10^{-6} s^{-1}) [34]. Similar lability has been found in the corresponding Rh_3 carboxylate complex over that of the hexaaqua species [35] and has been attributed to a *trans* labilising effect from the planar μ_3-oxo group. The present crystal structure of $[Ru_3O(CH_3CO_2)_6(OH_2)_3]^+$ reveals an averaged

Ru–O(OH_2) distance of 2.091 Å which may be compared with the average Ru–OH_2 distance in $[Ru(OH_2)_6]^{3+}$ (2.029 Å) [36]. The observed elongation may be the direct result of the *trans* labilising effect from μ_3-oxo ligand while at the same time leading to promotion of the I_d pathway. Different *trans* labilising effects arising from the μ_3-ligand have been invoked to explain the widely differing CD_3OD substitution rates occurring between the trimolybdenum species $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^{2+}$ and $[Mo_3(\mu_3\text{-}O)(\mu CCH_3)(\mu\text{-}CH_3CO_2)_6(OH_2)_3]^{2+}$ (non-planar μ_3-ligands) with the latter reacting $10^5\times$ faster [37]. The conclusion was that the μ_3-CCH_3 ligand exerts a larger *trans* effect than the μ_3-oxo ligand. This was reflected in average Mo–O(OH_2) distances for the μ_3-CCH_3 complex (2.177 Å) [38] being significantly longer than those for the corresponding μ_3-oxo complex (2.106 Å) [39]. An unusually long Cr–F bond has been recently reported in the structure of $[Cr_3O(CH_3CO_2)_6F_3]^{2-}$ suggestive also of a significant *trans* effect from the μ_3-oxo ligand [40]. In the triiridium(III,IV,IV) complex $[Ir_3(\mu_3\text{-}N)(\mu\text{-}SO_4)_6(OH_2)_3]^{4-}$ significant *trans* labilisation of the water ligands arising from the planar μ_3-nitrido ligand has also been detected [41] although here the Ir–OH_2 distance (2.059 Å) is not particularly exceptional [42].

Finally, the importance of *trans* labilisation from the planar μ_3-oxo ligand in promoting an I_d mechanism for substitution on $[Ru_3O(CH_3CO_2)_6L_3]^+$ is evident when one compares with the considerable evidence for associative I_a activation in mononuclear complexes of Ru(III) [43–46] such as $[Ru(NH_3)_5(OH_2)]^{3+}$ (($\Delta V^{\ddagger}_{H_2O} = -4.0$ cm^3 mol^{-1}) [45], $[Ru(EDTA)(OH_2)]^-$ ($\Delta V^{\ddagger}_{NCS-\text{anation}} = -9.6$ cm^3 mol^{-1}) [46] and $[Ru(OH_2)_6]^{3+}$ ($\Delta V^{\ddagger}_{H_2O} = -8.3$ cm^3 mol^{-1}) [34].

Supplementary material

Tables of rate constants, H atom coordinates and isotropic displacement coefficients, Ru anisotropic displacement coefficients and remaining bond lengths and angles are available from the authors on request.

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