Equilibria in Complexes of *N*-Heterocyclic Molecules. Part 8.† Reaction of Tris(5-nitro-1,10-phenanthroline)ruthenium(II) Cation with Methoxide and Ethoxide Ions

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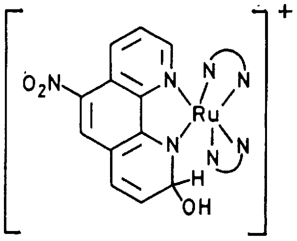
Spectroscopic studies show that methoxide ion reacts reversibly with methanolic solutions of the tris(5-nitro-1,10-phenanthroline)ruthenium(II) cation, $[RuL_3]^{2+}$, *via* addition to the 2 position of each heterocyclic ligand. An analogous addition occurs with ethoxide ion in ethanol, except that with excess of $[OEt]^-$ the diethoxy-adduct is precipitated. The kinetics of addition of the first alkoxide ion have been examined in both cases. With methoxide ion the observed rate law, Rate = $k_1[Ru][OMe^-] + k_{-1}[Ru]$, allows evaluation of both forward and reverse rate constants. For ethoxide ion a simple second-order rate law, Rate = $k_1[Ru][OEt^-]$, is observed. Comparison with similar data for the related additions of $[OH]^-$ and $[CN]^-$ ions to $[RuL_3]^{2+}$ shows the relative rate order $[OEt]^- > [OMe]^- \gg [OH]^- \gg [CN]^-$.

WE recently reported[1-6] several interesting spectroscopic changes for complexes of di-imine ligands with Pt^{II}, Pd^{II}, Fe^{II}, and Ru^{II}. We attribute these changes to attack at the ligand by nucleophiles such as $[OH]^-$ and $[CN]^-$. Of particular interest is the reversible reaction[4,5] of tris(5-nitro-1,10-phenanthroline)ruthenium(II), $[RuL_3]^{2+}$, with hydroxide ion, in which a monohydroxy-compound was shown to be initially formed by addition of $[OH]^-$ at the 9 position[5] of one ligand as in (1). Cyanide ion was shown[6] to react with $[RuL_3]^{2+}$ in an analogous fashion to form, in the first instance, a $[CN]^-$-substituted ligand at either the 2 or 9 position.



(1)

This adduct in the presence of more concentrated $[CN]^-$ then adds[6] another cyanide ion to form a neutral species. These reactions are summarised in equations (1)—(3).

$$[RuL_3]^{2+} + [OH]^- \longrightarrow [Ru(LOH)L_2]^+ \quad (1)$$

$$[RuL_3]^{2+} + [CN]^- \longrightarrow [Ru(LCN)L_2]^+ \quad (2)$$

$$[Ru(LCN)L_2]^+ + [CN]^- \longrightarrow [Ru(LCN)_2L] \quad (3)$$

Reversible u.v.–visible spectral changes analogous to those observed with the $[OH]^-$ and $[CN]^-$ cases also occur when $[RuL_3]^{2+}$ is dissolved in alcoholic solutions containing ethoxide or methoxide ions. The reactions of $[RuL_3]^{2+}$ with alkoxide ions have now been examined in detail using a variety of spectroscopic techniques, and the product has been isolated in the ethoxide case. In both cases addition of alkoxide ion to the co-ordinated 5-nitro-1,10-phenanthroline is confirmed. Kinetic data are reported for both alkoxide-addition processes.

EXPERIMENTAL

Materials.—The complex $[RuL_3]Cl_2\cdot6H_2O$ was prepared by the published route[6] except that it was eluted from the Sephadex C-25 cation-exchange resin with 0.1 mol dm^{-3} LiCl.

The product from the reaction of $[RuL_3]^{2+}$ with $[OEt]^-$ could be prepared from *saturated* solutions of the parent complex in EtOH by the following method. To a saturated solution of $[RuL_3]^{2+}$ in EtOH (25 cm^3) was added a solution (10 cm^3) of Na[OEt] in EtOH prepared by dissolving Na (0.5 g) in EtOH (50 cm^3). A precipitate was formed after a few minutes and was filtered at the pump and dried at room temperature *in vacuo* [Found: C, 55.8; H, 3.5; N,

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† Part 7 is ref. 6.

[1] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.

[2] E. Bielli, P. M. Gidney, R. D. Gillard, and B. T. Heaton, *J.C.S. Dalton*, 1974, 2133.

[3] E. Bielli, R. D. Gillard, and T. D. W. James, *J.C.S. Dalton*, 1976, 1837.

[4] R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51.

[5] R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, unpublished work.

[6] R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 226.

14.0. Calc. for $C_{40}H_{31}N_9O_8Ru$ (*viz.* the neutral diethoxy-adduct): C, 55.4; H, 3.6; N, 14.5%]. The related methoxide adduct could not be precipitated from methanolic solutions of methoxide, presumably because of this complex's much greater solubility in methanol.

The methanol and ethanol used for these experiments as well as for all the kinetic studies were dried through the well known Grignard procedure [7] and stored over molecular sieves.

Infrared spectra (KBr discs) were recorded using a Perkin-Elmer 257 grating spectrophotometer, electronic spectra with a Pye–Unicam SP 8000 recording spectrophotometer, and ^1H n.m.r. spectra with a Perkin-Elmer R32 spectrometer. For the n.m.r. studies, [$^2H_6$]ethanol and [$^2H_4$]methanol were used, and solutions containing [$^2H_5$]ethoxide and [$^2H_3$]methoxide were prepared by adding a known amount of sodium to the appropriate deuteriated alcohol. Chemical shifts were measured relative to $SiMe_4$ as internal standard.

Kinetic Studies.—Freshly prepared solutions of nucleophile were made by adding freshly cut sodium to known volumes of alcohol. Titration with standardised HCl using phenolphthalein as indicator yielded accurate concentrations of nucleophile. For all the kinetic runs, sufficient complex was weighed out to give $[RuL_3^{2+}] = 1.0 \times 10^{-5}$ mol dm^{-3}, and the ionic strength was maintained at 0.10 mol dm^{-3} by the addition of appropriate amounts of NaI.

The reactions were too fast to follow by conventional methods and a stopped-flow spectrophotometric technique was employed. The design of the instrument [8] eliminates thermostatting problems common to most other designs by using a glass-enclosed assembly of quartz light guides, observation port, and mixer. A strong visible light source was provided by a Bausch and Lomb high-intensity monochromator fitted with variable slits. The alkoxide reactions were generally followed at 380 nm, at which wavelength a large increase in absorbance is observed. In a few cases the reactions were also monitored at 500 nm (the spectral intensity decreasing at this wavelength) as a check. Reaction traces were recorded and stored on a Tektronix 564B storage oscilloscope fitted with a log-converter, thus affording a direct record of absorbance change with time. Pseudo-first-order rate constants were determined from plots of $\log(A_\infty - A_t)$ against time, the absorbances being assigned arbitrary units.

RESULTS AND DISCUSSION

The Nature of the Alkoxide Reactions.—The electronic spectra of $[RuL_3]^{2+}$ ([complex] = 1.0×10^{-5}—2.0×10^{-5} mol dm^{-3}) in EtOH, and on addition of $[OMe]^-$ and $[OEt]^-$ ions (p[OR^-] 3) are shown in Figure 1. It is noteworthy that under these conditions the spectra of the products are very similar. These product spectra were measured immediately after addition of alkoxide and it is therefore evident that the initial reaction in both alkoxide cases is the same. Under the dilute conditions employed for the above spectral measurement, precipitation of the ethoxide adduct was avoided. It is obvious that the ligand band near 270 nm arising from exciton coupling of the identical aromatic ligands is diminished on addition of alkoxide, suggesting that the ligand(s) has undergone a reaction similar to those previously found [4-6] involving $[OH]^-$ and $[CN]^-$. The spectroscopic changes described above are reversible. Not only did the addition of dilute acid cause reversal of

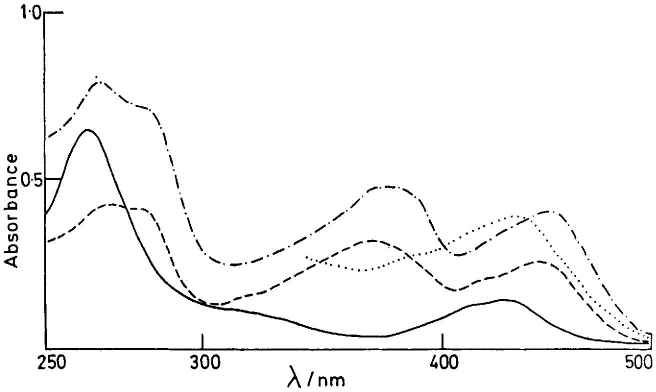

FIGURE 1 Electronic spectra: (——), $[RuL_3]^{2+}$ (1.0×10^{-5} mol dm^{-3}) in EtOH; (– – – –), $[RuL_3]^{2+}$ (1.0×10^{-5} mol dm^{-3}) in MeOH with p[OMe^-] 3; (— · — · —), $[RuL_3]^{2+}$ (2.0×10^{-5} mol dm^{-3}) in EtOH with p[OEt^-] 3; and (· · · ·), the diethoxy-adduct (2.0×10^{-3} mol dm^{-3}) dissolved in EtOH

TABLE 1

Hydrogen-1 n.m.r. chemical shifts (p.p.m.) and coupling constants (Hz) measured at 90 mHz [a]

Complex	Solvent	
$[RuL_3]^{2+}$	CD_3OD [b]	2, d, 8.96, 9.5; 3, t, 7.85, 9.2;[c] 4, d, 8.02, 9.0;[d] 6, s, 9.32, 4.1; 7, d, 8.42, 9.0;[d] 8, t, 7.96, 9.2;[c] 9, d, 9.22, 9.0. $J(H^2H^3)$ 8.0, $J(H^8H^9)$ 9.0, $J(H^3H^4) \approx J(H^7H^8) \approx 5$, $J(H^2H^4) \approx J(H^7H^9) < 1$
$[RuL_3]^{2+}$	CD_3CD_2OD [b]	2, d, 9.00, 7.3; 3, t, 7.96, 7.3;[e] 4, d, 8.42,[f] 7.5; 6, s, 9.34, 7.6; 7, d, 8.42,[f] 7.5; 8, t, 8.05, 7.3;[e] 9, d, 9.21, 7.1. $J(H^2H^3)$ 7.0, $J(H^8H^9)$ 9.5, $J(H^3H^4) \approx J(H^7H^8) \approx 5$, $J(H^2H^4) \approx J(H^7H^9) < 1$
$[RuL_3]^{2+}$	CD_3OD–CD_3O^- [g]	9.35, 8.12, 7.39, 6.47
$[RuL_3]^{2+}$	CD_3OD–CD_3O^- [h]	2, s (br), 6.48, 5.5; 6, s, 9.47, 6.8; 9, d, 9.36, 5.0. $J(H^8H^9) \approx 6$. Remainder of signals are broad: 8.20, 7.97, 7.70, 7.47, 7.28. Average signal area of each remaining proton (assuming 4) 7.0
i	CD_3OD–CD_3O^-	8.88, d, 4.5, *J* 8.4; 8.56, d, 4.5, *J* 8.4; 8.14, d, 4.6, *J* 5.3; 7.84, d, 5.0, *J* 4.8; *ca.* 7.69, m, 14.1;[j] 7.61, s, 7.1 [j]

[a] Results are given in the order: proton number (where assignment is possible), splitting pattern, chemical shift, and peak area. Coupling constants are given after the chemical-shift data. [b] Saturated solution at 35 °C. [c] Superimposed triplets of total area 18.4. [d] Superimposed doublets of total area 18.0. [e] Superimposed triplets of total area 14.3. [f] Unresolved signal of total area 15.0. [g] $[CD_3O^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, 35 °C. Chemical shifts only of the centres of broad signals are given. [h] $[CD_3O^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, −48 °C. [i] $[CD_3O^-] = 1.0 \times 10^{-3}$ mol dm^{-3} initially. Spectrum is of final reaction product after 12 h (see text). Results are given in the order: chemical shift, splitting pattern, peak area, coupling constant (if measurable). [j] Sum of areas = 21.2.

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[7] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966.

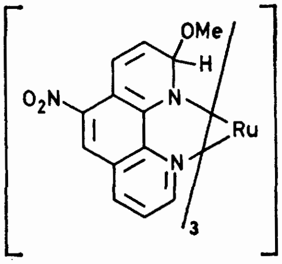
[8] D. Michael, D. O'Donnell, and N. H. Rees, *Rec. Sci. Instrument*, 1974, **45**, 256.

the spectra to that of $[RuL_3]^{2+}$ alone, but dilution of the reaction mixtures with OEt_2 afforded 100% recovery of $[RuL_3]Cl_2$, which on drying *in vacuo* and redissolving in alcohol yielded its characteristic spectrum.

The nature of these novel processes was further elucidated by ^1H n.m.r. studies. The spectra of $[RuL_3]^{2+}$ in $[^2H_6]$ethanol and $[^2H_4]$methanol are given in Table 1. The complex is much less soluble in EtOH than in MeOH and the spectrum in the former solvent could be obtained only at the most sensitive setting of the instrument. Small changes in chemical shifts and coupling constants were observed which are in accord [9] with the slightly different hydrogen-bonding properties of the two solvents. The spectra were assigned on the basis of spin-decoupling experiments and by comparison with the spectra [2,10-15] of complexes containing other substituted 1,10-phenanthrolines. The assignment of the chemical shifts of H^2 and H^9 (and hence of other protons in the corresponding rings) derives from consideration of the resonance hybrids of the ligand molecule; the 9 position, which is *para* to the 5-nitro-group, is expected to be the more deshielded and hence the signal for H^9 is expected at slightly lower field than the signal for H^2.

Addition of $[^2H_5]$ethoxide to the saturated $[^2H_6]$-ethanol solution of $[RuL_3]^{2+}$ gave a precipitate (p$[OR^-]$ 3) and it was not possible to measure the spectrum of any product formed. However, on addition of $[^2H_3]$-methoxide (p$[OR^-]$ 3) to the methanolic solution, the spectrum shown in Table 1 was obtained. Also shown is the better resolved spectrum which was obtained when the reaction mixture was cooled to −48 °C; here, some of the signals could be assigned. While the temperature-dependent broadening of the spectrum is consistent [9] with a relatively mobile equilibrium, as shown by kinetic studies (see below), some peaks at −48 °C were sharp. The H^6 and H^9 signals were resolved, having chemical shifts of 9.47 and 9.36 p.p.m. respectively $[J(H^8H^9)$ *ca.* 6 Hz$]$. These values are comparable to those in the parent complex of 9.32 and 9.22 p.p.m. $[J(H^8H^9)$ 9.0 Hz$]$. The most striking feature of the spectrum is, however, the complete disappearance of the signal at 8.96 p.p.m. assigned to H^2, and the appearance of a new high-field proton at 6.48 p.p.m. We attribute this change in spectrum to the addition of a methoxide ion to the 2 position of the ligand, and since the signals are quantitatively transposed it seems that each of the ligands has undergone attack to yield the structure (2). This initial adduct is stable for some hours, but on prolonged standing a new product is formed with the spectrum shown in Table 1 (*i*). The exact nature of this latter product is not understood at present.

It is somewhat surprising that $[OMe]^-$ adds to the 2 position, since hydroxide ion appears to react with the 9 position of the same complex. It is noted that the 2 position is less (although slightly) electrophilic than the 9 position. However, other instances of different nucleophiles adding to different positions of a coordinated molecule are known.[16] It is unfortunately impossible to compare the site of $[OMe]^-$ attack with that in the $[CN]^-$ case, since in this latter the adduct is virtually insoluble [6] and its n.m.r. spectrum could not be recorded.



(2)

Burgess and Prince [17] postulated that, in base, 5-nitro-1,10-phenanthroline both as a ligand and as the free molecule loses the H^6 proton. However, the retention of the H^6 signal both in the present methoxide reaction (Table 1) and in the case [5] of $[OH]^-$ attack means that in these reactions at least the loss of H^6 does not occur. Furthermore, there is no deuterium exchange observed [1,3,4] on repeated reversal of the reaction with acid and base in the $[OH]^-$ example. In order to establish beyond doubt the fact that there is no exchange, $[RuL_3]^{2+}$ was treated with $[^2H_5]$ethoxide in $[^2H_6]$ethanol and the solid obtained was dissolved in D_2O containing a trace amount of DCl. Addition to a D_2O solution of $Na[ClO_4]$ yielded the original $[RuL_3]^{2+}$ complex as its perchlorate salt. There was no evidence for C–D bonds in the i.r. spectrum.

Although it was not possible to measure the n.m.r. spectrum of the reaction mixture obtained on adding $[OEt]^-$ to $[RuL_3]^{2+}$, the product isolated (see Experimental section) was the diethoxy-adduct. When the solid product is dissolved in EtOH it gives the characteristic spectrum shown in Figure 1. In the visible region, $\lambda_{max.} = 462$ nm, which is intermediate between that of $[RuL_3]^{2+}$ ($\lambda_{max.}$ 451 nm) and the reaction mixture containing excess of $[OEt]^-$ ($\lambda_{max.}$ 478 nm). Since it is known that the addition of $[OEt]^-$ involves an equilibrium, these results simply reflect the partial dissociation of $[OEt]^-$ from the complex adduct in an equilibrium fashion.

The i.r. spectra of $[RuL_3]Cl_2$ and the diethoxy-adduct are shown in Figure 2. The new bands present in the adduct, some of which are assignable to aliphatic C–H and aromatic ether stretching frequencies, together with

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[9] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1.

[10] J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 1965, 3185.

[11] J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 1965, 4706.

[12] J. A. Summers, *Tetrahedron*, 1968, **24**, 5433.

[13] J. D. Miller and R. H. Prince, *J. Chem. Soc.* (*A*), 1969, 519.

[14] G. C. Kulasingam, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc.* (*A*), 1969, 521.

[15] J. V. Rund and P. C. Keller, *J. Chem. Soc.* (*A*), 1970, 2827.

[16] P. L. Pauson and K. H. Todd, *J. Chem. Soc.* (*C*), 1970, 2638.

[17] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

the changes in the aromatic band at *ca.* 665 cm^{-1}, indicate that the reaction between $[RuL_3]^{2+}$ and $[OEt]^-$ involves attack at the ligand. Because of the strikingly similar electronic spectra, it appears that the attack is analogous to that with $[OMe]^-$. The structure of the product, which is very insoluble in EtOH, is suggested as (3). No attempt was made to differentiate between the 2 or 9 position as the site of attack.

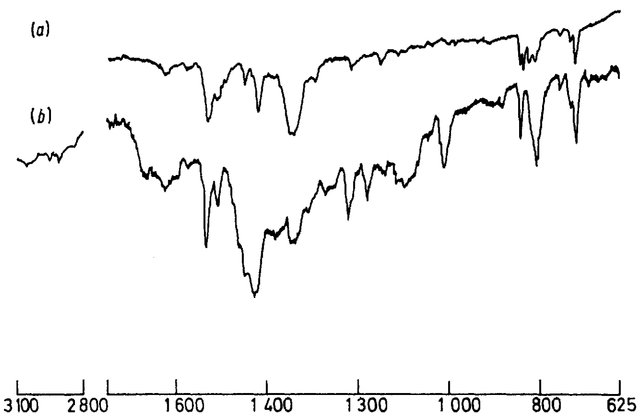
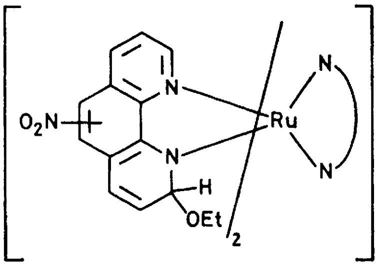


FIGURE 2 Infrared spectra (KBr disc) of (*a*) $[RuL_3]Cl_2{\cdot}6H_2O$ and (*b*) the diethoxy-adduct



(3)

Kinetic Studies.—The kinetics of the alkoxide additions to $[RuL_3]^{2+}$ were followed using a large excess of nucleophile. Under these conditions linear first-order kinetics were invariably obeyed for at least three half-lives.

Methoxide addition. The kinetic results for the reaction of $[OMe]^-$ with $[RuL_3]^{2+}$ are given in Tables 2 and 3. Individual $k_{obs.}$ values are the average of triplicate determinations with a reproducibility of $\pm 5\%$. At each particular temperature a plot of $k_{obs.}$ against $[OMe^-]$ was linear with a non-zero intercept, indicating the general rate equation (4). This rate equation may be explained by either of the equilibrium processes (5) or (6)—(8).

$$k_{obs.} = k_a[OMe^-] + k_b \qquad (4)$$

(*i*) In this case k_a and k_b in (4) refer to the forward and reverse rate constants k_1 and k_{-1}, respectively, for addition of the first methoxide ion.

$$[RuL_3]^{2+} + [OMe]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(LOMe)L_2]^+ \qquad (5)$$

Such behaviour implies that, under the conditions of the kinetic experiments ([Ru] *ca.* 1×10^{-5} mol dm^{-3}; $[OMe^-] \leqslant 0.1$ mol dm^{-3}), further additions of methoxide ion to the complex [equation (7) and (8) below] are very much slower than k_1 (as expected from an electrostatic viewpoint) and/or additions (7) and (8) are equilibria which lie far to the left.

TABLE 2

Kinetic data for the reaction of $[RuL_3]^{2+}$ with methoxide ion in methanol

$\frac{[OMe^-]}{mol\ dm^{-3}}$	$\frac{T}{K}$	$\frac{k_{obs.}}{s^{-1}}$
0.007	299.0	19.9
0.014	299.0	25.7
0.021	299.0	29.5
0.028	299.0	32.4
0.035	299.0	36.1
0.042	299.0	40.4
0.049	299.0	44.1
0.056	299.0	49.7
0.140	299.0	96.5
0.010	292.8	15.7
0.030	292.8	21.1
0.060	292.8	35.9
0.100	292.8	49.9
0.010	286.2	9.1
0.030	286.2	12.2
0.060	286.2	20.4
0.100	286.2	27.9
0.010	279.8	6.3
0.030	279.8	7.5
0.060	279.8	11.7
0.100	279.8	21.2
0.010	273.3	3.4
0.030	273.3	4.2
0.060	273.3	6.4
0.100	273.3	12.2

TABLE 3

Forward and reverse rate constants and thermodynamic parameters for the reaction of $[RuL_3]^{2+}$ with methoxide ion in methanol

$\frac{T}{K}$	$\frac{k_1}{dm^3\ mol^{-1}\ s^{-1}}$	$\frac{k_{-1}}{s^{-1}}$
299.0	608 (5)	15.1 (0.9)
292.8	384 (21)	11.3 (1.5)
286.2	215 (14)	6.6 (1.6)
279.8	165 (22)	3.5 (1.3)
273.3	99 (17)	1.6 (1.0)

$\Delta H_1^{\ddagger} = 44.5$ (0.2) kJ mol^{-1}, $\Delta H_{-1}^{\ddagger} = 57.0$ (1.8) kJ mol^{-1}, $\Delta H^{\ominus} = -12.5$ (2.0) kJ mol^{-1}, $\Delta S_1^{\ddagger} = -43$ J K^{-1} mol^{-1}, $\Delta S_{-1}^{\ddagger} = -30$ (2) J K^{-1} mol^{-1}, $\Delta S^{\ominus} = -13$ (3) J K^{-1} mol^{-1}.

(*ii*) In this instance k_a and k_b refer to the forward and reverse rate constants k_3 and k_{-3} for addition of the third methoxide ion.

$$[RuL_3]^{2+} + [OMe]^- \xrightarrow{\text{fast}} [Ru(LOMe)L_2]^+ \qquad (6)$$

$$[Ru(LOMe)L_2]^+ + [OMe]^- \xrightarrow{\text{fast}} [Ru(LOMe)_2L] \qquad (7)$$

$$[Ru(LOMe)_2L] + [OMe]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ru(LOMe)_3]^- \qquad (8)$$

Scheme (*ii*) is consistent with the complete disappearance of the n.m.r. signal of the H^2 proton of $[RuL_3]^{2+}$ on addition of excess of methoxide ions. However, this scheme can be eliminated since extrapolation of stopped-flow data back to zero time gave absorbance values expected for the original complex $[RuL_3]^{2+}$. The single addition scheme (*i*) is therefore favoured for the kinetic experiments. It is apparently only at the high complex and methoxide-ion concentrations employed in the n.m.r. experiments that the kinetically and/or thermodynamically unfavourable second and third additions (7) and (8) are observed. Under the kinetic conditions of Table 2 the A_∞ values for each run remained constant for several minutes, giving no evidence for subsequent reactions. The A_∞ values did, however, increase with increasing [OMe⁻], as expected for an equilibrium reaction.

TABLE 4

Kinetic and thermodynamic parameters for the reaction of $[RuL_3]^{2+}$ with ethoxide ion in ethanol

$\frac{[OEt^-]}{\text{mol dm}^{-3}}$	$\frac{T}{\text{K}}$	$\frac{k_{obs.}}{\text{s}^{-1}}$
0.005	299.5	15.5
0.010	299.5	33.8
0.020	299.5	58.2
0.040	299.5	128.9
0.010	304.5	47.7
0.010	293.2	24.2
0.010	288.3	15.2
0.010	283.1	9.8
0.010	277.8	6.5

k_1 = 3 190 (108) dm³ mol⁻¹ s⁻¹ at 299.5 K; $\Delta H_1^\ddagger$ = 46.6 (5.2) kJ mol⁻¹, $\Delta S_1^\ddagger$ = −29 (2) J K⁻¹ mol⁻¹.

Methoxide attack on $[RuL_3]^{2+}$ is therefore very similar to that by cyanide ion, which has also been shown [6] to usually involve a single addition to give $[Ru(LCN)L_2]^+$. Further cyanide addition, leading to precipitation of insoluble $[Ru(LCN)_2L]$, only occurred at very high [Ru] and/or [CN⁻]. Similarly, reaction of $[RuL_3]^{2+}$ with [OH]⁻ has been shown [4,5] to involve rapid addition of one hydroxide ion, followed by much slower subsequent processes.

The values for k_1 and k_{-1} in Table 3 were obtained by the usual least-squares techniques. Values of $\Delta H_1^\ddagger$ and $\Delta H_{-1}^\ddagger$ were determined *via* least-squares analyses of Arrhenius plots of k_1 and k_{-1} data, respectively. The errors quoted are the standard deviations obtained in the least-squares procedure. Values of $\Delta S_1^\ddagger$ and $\Delta S_{-1}^\ddagger$ were calculated using second- and first-order rate constants, respectively. The standard enthalpy and entropy changes for equilibrium (5) were estimated from the relations $\Delta H^\ominus = \Delta H_1^\ddagger - \Delta H_{-1}^\ddagger$ and $\Delta S^\ominus = \Delta S_1^\ddagger - \Delta S_{-1}^\ddagger$.

The rapid addition, k_1, of the first methoxide ion is seen (Table 3) to arise from the relatively low value of $\Delta H_1^\ddagger$. The negative entropy of activation for the forward reaction is also as expected for an addition process. However, the negative $\Delta S_{-1}^\ddagger$ value for the reverse dissociative process is unexpected, and suggests that solvation of the transition state is significant in this reaction.

Combination of k_1 and k_{-1} data at 25 °C gives an equilibrium constant K (= k_1/k_{-1}) of 40 dm³ mol⁻¹ (Table 5). Equilibrium (5) is seen to be only slightly exothermic; the $\Delta H^\ominus$ value of −12.5 kJ mol⁻¹ must reflect not only the formation of a C–O bond, but also the disruption of the aromaticity of a ligand molecule, as well as solvation changes. While $\Delta S^\ominus$ is negative as anticipated, the relatively small value again supports the presence of significant (but not dominant) solvation effects.

TABLE 5

Forward rate constants and thermodynamic parameters for the reaction of $[RuL_3]^{2+}$ with various nucleophiles

Nucleophile (solvent)	$\frac{k_1\ (37\ °\text{C})}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	$\frac{\Delta H_1^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S_1^\ddagger}{\text{J K}^{-1}\ \text{mol}^{-1}}$	$\frac{K = k_1/k_{-1}}{\text{dm}^3\ \text{mol}^{-1}}$
[OH]⁻ (Water) [a]	18.7			149
[CN]⁻ (Water) [b]	0.16	51.3 (6.1)	−94 (18)	*c*
[OMe]⁻ (Methanol)	1 200 [d]	44.5 (0.2)	−43 (1)	40
[OEt]⁻ (Ethanol)	6 000 [d]	46.6 (5.2)	−29 (2)	>250

[a] From ref. 4. [b] From ref. 6. [c] Very large. [d] Calculated from Arrhenius plots.

Ethoxide addition. Kinetic data for the reaction of ethoxide ion with $[RuL_3]^{2+}$ are collected in Table 4. The rate constants are again the average of triplicate determinations, with reproducibility ±5%. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from the usual Arrhenius plot, the errors quoted being the standard deviations derived from the least-squares analysis.

Unlike the methoxide reaction, a plot of $k_{obs.}$ against [OEt⁻] passed through the origin, and obeyed the simple second-order rate equation (9). This rate

$$k_{obs.} = k[OEt^-] \qquad (9)$$

equation is most readily rationalised in terms of rate-determining addition of an [OEt]⁻ ion to $[RuL_3]^{2+}$, *i.e.* equation (10). Alternative mechanisms involving rapid

$$[RuL_3]^{2+} + [OEt]^- \xrightarrow{k_1} [Ru(LOEt)L_2]^+ \qquad (10)$$

addition of the first [OEt]⁻ ion followed by subsequent rate-determining addition, such as in scheme (*ii*), are eliminated by the failure (as in the methoxide case) to observe any spectral intermediates.

Within their standard deviations, the $\Delta H_1^\ddagger$ values for the [OEt]⁻ (Table 4) and [OMe]⁻ (Table 3) reactions are the same, supporting a similar mechanism in each case. A negative $\Delta S_1^\ddagger$ is also observed for [OEt]⁻, as expected for an addition process. It is noteworthy that addition of diethyl ether to reaction mixtures shows that reaction (10) is in fact reversible (see above). Thus, assuming a more general rate equation of the type (4) for the ethoxide reaction, a least-squares analysis of the data led to a k_{-1} value of −0.6 ± 12.8 s⁻¹. Assuming a maximum of 12.2 s⁻¹ for k_{-1}, gave rise to a minimum K (= k_1/k_{-1}) value of 250 dm³ mol⁻¹ for [OEt]⁻ at 25 °C (Table 5).

Comparison of alkoxide ions with other nucleophiles. The present kinetic data for the alkoxide reactions (5) and (10) may be compared with results previously obtained [4-6] for the analogous monoadditions of $[OH]^-$ and $[CN]^-$ ions to the 5-nitro-1,10-phenanthroline ligand in $[RuL_3]^{2+}$. Table 5 summarises the available data.

While a strict comparison of the rates is prevented by the different solvents involved, the data indicate a strong decrease in nucleophilicity towards $[RuL_3]^{2+}$ down the order $[OEt]^- > [OMe]^- \gg [OH]^- \gg [CN]^-$ ($3.7 \times 10^4 : 7.5 \times 10^3 : 1.2 \times 10^2 : 1$). This very striking dependence of the rate on the nature of the nucleophile is remarkable for an octahedral metal complex, and further supports our contention that nucleophilic attack is occurring at the organic ligand. In contrast, Burgess [18] reported similar second-order rate constants for displacement of the 5-nitro-1,10-phenanthroline ligand in $[FeL_3]^{2+}$ by $[OH]^-$ and $[CN]^-$ (0.29 and 0.51 $dm^3\ mol^{-1}\ s^{-1}$ at 35 °C, respectively), a process involving attack at the metal. (Furthermore, the rate of attack of $[CN]^-$ at the iron centre in $[FeL_3]^{2+}$ is similar in water and alcohols.) Interestingly, the rate sequence $[OMe]^-$ (methanol) $\gg$ $[OH]^-$ (water) $>$ $[CN]^-$ (water) has also been recently reported by Ritchie [19] for addition of nucleophiles to free carbonium ions.

The marked differences in rate with nucleophile are not reflected in the $\Delta H_1^\ddagger$ values, which are the same within experimental error for $[OEt]^-$, $[OMe]^-$, and $[CN]^-$. For these three nucleophiles the relative rates are seen to be largely controlled by $\Delta S_1^\ddagger$; *e.g.* the very slow rate for $[CN]^-$ compared to the alkoxides arises from its much more negative $\Delta S_1^\ddagger$.

Another striking feature of the additions in Table 5 is the lack of correlation between rate and equilibrium constants. Cyanide and hydroxide ions, although relatively slow nucleophiles, have very much greater equilibrium constants (K) for addition than does the fast methoxide ion. This behaviour closely resembles that observed by Ritchie [19] for addition to free carbonium ions and may indicate an early transition state for these additions.

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