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THE REDUCTION OF DIOXOTETRACHLORORUTHENATE(VI) TO HEXACHLORORUTHENATE(IV) IN A BASIC 1-BUTYLPYRIDINIUM CHLORIDE–ALUMINIUM(III) CHLORIDE IONIC LIQUID*

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Abstract—The anion $[RuO_2Cl_4]^{2-}$ is sufficiently stable in a basic [*N*Bupy]Cl–$AlCl_3$ ([*N*Bupy] = 1-butylpyridinium) ionic liquid (44.44 mol% $AlCl_3$) at ambient temperature to enable its solution electronic absorption spectrum to be recorded for the first time, but is slowly reduced ($k = 1.45\times10^{-5}s^{-1}$; $t_{1/2} = 13.3$ h) in a pseudo-first-order process to give predominantly $[RuCl_6]^{2-}$, according to $[RuO_2Cl_4]^{2-}+2[AlCl_4]^- \rightarrow [RuCl_6]^{2-}+2''[AlOCl_2]^-{}''+Cl_2$. A by-product of the reduction process was tentatively identified as $[Ru_2OCl_{10}]^{4-}$, and was believed to be formed according to $2[RuO_2Cl_4]^{2-}+3[AlCl_4]^- \rightarrow [Ru_2OCl_{10}]^{4-}+3''[AlOCl_2]^-{}''+2Cl_2$. This is the first documented irreversible transfer of an oxide ion from an isolable transition metal complex to tetrachloroaluminate in an ambient-temperature ionic liquid.

The salts $A_2[RuO_2Cl_4]$ (A = Rb or Cs) were first described by Howe in 1901,[1] and the synthetic routes to these complexes were later improved by Woodhead and Fletcher.[2] The known chemical and physical properties of these salts have been reviewed elsewhere,[3,4] but, to date, the spectroscopic properties of the dioxotetrachlororuthenate(VI) anion have been rather poorly characterized. Ten years ago, an important paper appeared[5] describing the formation of the novel salts $A[RuO_2Cl_3]$ (A = $[PPh_4]$ or $[AsPh_4]$), which now have a widespread utility as organic oxidants (converting alcohols to aldehydes and ketones, without attacking C=C double bonds).[6] The green anion in these salts was tentatively described as a dimeric species, $[Ru_2O_4Cl_6]^{2-}$, in the solid state but as a monomer, $[RuO_2Cl_3]^-$, in solution:[5] it is now known to be

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* This paper is dedicated to Prof. E. W. Abel, who provided me (K.R.S.) with help and support when it was most needed, in recognition of his lifetime interest in, and contributions to, ruthenium chemistry. And, yes, Eddie, I still have the picture (and negative) of you wielding two large sticks over a group of cavorting ladies in exotic dress.

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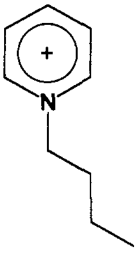
five-coordinate in both solution and the solid state, although its precise geometry is cation dependent.[7]

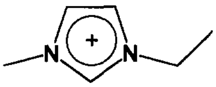
Two features of the chemistry of $[RuO_2Cl_4]^{2-}$ that have prevented its spectroscopic characterization have been its apparent instability in solution in the absence of dichlorine, and the availability of at least two distinct decomposition pathways, namely eqs (1) and (2).[1,8]

$$2[RuO_2Cl_4]^{2-}+6H_2O \longrightarrow [RuO_4]+RuO_2+8Cl^-+4[H_3O]^+ \quad (1)$$

$$[RuO_2Cl_4]^{2-}+4[H_3O]^+ +4Cl^- \longrightarrow [RuCl_6]^{2-}+6H_2O+Cl_2. \quad (2)$$



[*N*Bupy]$^+$



[emim]$^+$

The use of basic ambient-temperature ionic liquids (e.g. [emim]Cl–$AlCl_3$ and [*N*Bupy]Cl–$AlCl_3$; [emim] = 1-ethyl-3-methylimidazolium; [*N*Bupy] = 1-butylpyridinium) as solvents for transition metal chloride complexes is now becoming established, and is reviewed elsewhere.[9] One very interesting, but little understood, feature of these novel solvents is the chemistry associated with the oxide ion. Even at impurity levels, the following equilibrium, eq. (3), is believed to exist in basic melts (i.e. those which contain an excess of the organic chloride salt over aluminium(III) chloride):[10–13]

$$O^{2-}+[AlCl_4]^- \rightleftharpoons "[AlOCl_2]^-" +2Cl^-. \quad (3)$$

The description of the oxoaluminium(III) species as "$[AlOCl_2]^-$" is a convenient representation of a very complex situation, involving a plethora of oligomeric oxo-bridged species.[11,14,15] Furthermore, the presence of impurity oxide ion has considerably complicated electrochemical studies of $[TiCl_6]^{2-}$, owing to equilibrium (4), which is slowly established at room temperature:[16]

$$[TiCl_6]^{2-}+"[AlOCl_2]^-" \rightleftharpoons [TiOCl_4]^{2-}+[AlCl_4]^-. \quad (4)$$

A similar equilibrium was encountered in our own laboratories[17] when studying the $[MoCl_6]^{-/2-/3-}$ system. There are, however, no reported examples in which the reverse process has been observed, i.e. an isolable oxochloro complex of a transition metal irreversibly transferring its oxo ligand to chloroaluminate with the subsequent transfer of chloride ion. We describe here the improved syntheses and characterization of a number of $[RuO_2Cl_4]^{2-}$ salts, the first solution electronic absorption spectrum of $[RuO_2Cl_4]^{2-}$, the near quantitative reduction of $[RuO_2Cl_4]^{2-}$ to $[RuCl_6]^{2-}$ and the pseudo-first-order kinetics of that reduction.

EXPERIMENTAL

All experiments involving ionic liquids were performed in an inert atmosphere box filled with dry dinitrogen, and the basic [*N*Bupy]Cl–$AlCl_3$ ionic liquids (44.44 mol% $AlCl_3$) were prepared according to well-established procedures.[18] Electronic absorption spectra were recorded with a Perkin–Elmer PE 330 spectrophotometer connected, via an RS232C serial interface, with a Research Machines 380Z microprocessor. IR spectra were recorded with a Perkin–Elmer 580 spectrophotometer. Samples for IR spectroscopy were prepared as Nujol (sodium-dried) mulls between CsI discs, and IR spectra were calibrated with both a polystyrene film and indene. Microanalytical data were supplied by the Analytical Department of the Inorganic Chemistry Laboratory, Oxford University. $[AsPh_4]$ $[RuO_2Cl_3]$ was prepared according to the literature method.[5]

Preparation of hydrated ruthenium(IV) *oxide*

Commercial hydrated ruthenium(III) chloride (5 g) was dissolved in water (50 cm^3) and aqueous sodium hydroxide solution (*ca* 6 M; 200 cm^3) added. The black precipitate thus formed was collected by filtration, washed with distilled water (3 × 25 cm^3) and ethanol (25 cm^3) and dried *in vacuo* for 24 h.

Preparation of an aqueous solution of ruthenium(VIII) *oxide*

Ruthenium(VIII) oxide was prepared in small batches, as required, by the method of Nakata,[19] all operations being performed in a fume cupboard.

WARNING: *Solid ruthenium*(*VIII*) *oxide exerts a considerable vapour pressure at ambient temperatures, and its solutions readily lose* [RuO_4] *vapour even when kept at 0°C.* [RuO_4] *vapour has a choking odour and although its toxicological properties have not been fully studied, the material should always be handled in a fume cupboard, and protective rubber gloves worn to prevent skin contact.*

Hydrated ruthenium(IV) oxide (1 g) was mixed with solid sodium iodate(VII) (5 g) and ice-cold distilled water (*ca* 30 cm^3) was added. The cooled mixture was stirred until all the black material had been converted to ruthenium(VIII) oxide, leaving a clear, bright yellow solution. The ruthenium(VIII) oxide was then distilled from the solution (in an all-glass apparatus) by initially gently warming, and finally boiling, the solution in a stream of dinitrogen, and collecting the product below water (20 cm^3) at 0°C. The saturated solution of ruthenium(VIII) oxide thus formed was filtered through a sintered-glass disc and stored at 0°C before use. It was found to be stable for approximately 2 h under these conditions.

Preparation of a tetrachloromethane solution of ruthenium(VIII) *oxide*

A solution of ruthenium(VIII) oxide in tetrachloromethane was prepared in a similar manner to the aqueous solution, but instead of distilling the product, the solution was extracted with three equal (10 cm^3) portions of tetrachloromethane. The fractions were combined, and the resulting solution was stored at 0°C in contact with an upper layer of aqueous sodium iodate(VII) solution (1 g in *ca* 5 cm^3).

Preparation of caesium tetrachlorodioxoruthenate(VI)

This preparation of $Cs_2[RuO_2Cl_4]$ was based on the method of Howe,[1] observing the precautions suggested by Woodhead and Fletcher.[2]

Caesium chloride (5 g) and concentrated hydrochloric acid (2 cm^3) were added to a saturated aqueous solution of $[RuO_4]$ (20 cm^3) at room temperature. The vessel was left loosely covered at room temperature for a period of 24 h, during which time a dark purple–brown crystalline precipitate formed. The product was collected by filtration and rapidly washed with dichlorine-saturated hydrochloric acid (0.5 M : 2 × 5 cm^3), tetrachloromethane (5 × 5 cm^3), ethanol (2 × 5 cm^3) and diethyl ether (10 cm^3). The crystals were then transferred to a vacuum desiccator and stored over P_2O_5. Found: Cl, 26.1; Cs, 48.9; Ru, 18.5. Calc. for $Cl_4Cs_2O_2Ru$: Cl, 26.2; Cs, 49.2; Ru, 18.7%.

Preparation of rubidium tetrachlorodioxoruthenate(VI)

Purple crystalline $Rb_2[RuO_2Cl_4]$ was prepared by a method analogous to that used for the caesium salt. A larger quantity of rubidium chloride (10 g) was required to cause precipitation of the more soluble rubidium tetrachlorodioxoruthenate(VI). Found: Cl, 31.4%. Calc. for $Cl_4O_2Rb_2Ru$: Cl, 31.6%.

Preparation of caesium tetrabromodioxoruthenate(VI)

Caesium bromide (10 g) and concentrated hydrobromic acid (2 cm^3) were added to a saturated aqueous solution of ruthenium(VIII) oxide (20 cm^3) at room temperature. The solution immediately darkened and, after *ca* 2 min, a dark brown, almost black, precipitate formed. This was collected by filtration, washed with concentrated hydrobromic acid (1 cm^3), tetrachloromethane (5 × 5 cm^3), ethanol (2 × 5 cm^3) and diethyl ether (10 cm^3). The resulting dark brown powder was transferred to a vacuum desiccator and stored over P_2O_5. Found: Br, 45.2%. Calc. for $Br_4Cs_2O_2Ru$: Br, 44.5%.

RESULTS AND DISCUSSION

Characterization of the dioxotetrahaloruthenate(VI) *salts*

Although the dioxotetrahaloruthenate(VI) salts have been known since the turn of the century, there are still major discrepancies in the literature concerning the simple assignments of the IR-active vibrational modes of $[RuO_2X_4]^{2-}$ (X = Cl or Br). In two independent reports,[20,21] bands are reported at *ca* 320 cm^{-1} [assigned to $\nu_{as}(RuCl_4)$] and 305 cm^{-1} [assigned to $\delta(RuO_2)$] in the IR spectra of $[RuO_2Cl_4]^{2-}$ salts, whilst the spectra of $[RuO_2Br_4]^{2-}$ salts purportedly show bands at *ca* 309 cm^{-1}. We find (in accordance with Griffith's report[22] of the IR spectrum of $Cs_2[RuO_2Br_4]$) no IR-active bands in this region assignable to $\delta(RuO_2)$; our results are summarized in Table 1, along with the current literature assignments. These results place $\nu_{as}(RuO_2)$ at 824–829 cm^{-1} (with, in the case of both caesium salts, a slight splitting suggestive of a solid-state distortion away from regular D_{4h} symmetry), $\nu_{as}(RuCl_4)$ at 308 cm^{-1} and $\nu_{as}(RuBr_4)$ at 230 cm^{-1}. These assignments differ significantly from those of the Polish[20] and Russian[21] workers, raising some questions concerning the integrity of the report (no preparative details were provided, even for novel complexes) in the former case, and the purity of the products in the latter case. Nevertheless, even in the absence of a crystallographic study, these results provide persuasive evidence that the $[RuO_2X_4]^{2-}$ ions have a *trans* configuration, as found in their organic salts,[7] and like their osmium

Table 1. IR data for $A_2[RuO_2X_4]$ salts

A	X	$\nu_{as}(RuO_2)$ (cm^{-1})	$\nu_{as}(RuX_4)$ (cm^{-1})	$\delta(RuO_2)$ (cm^{-1})	
Cs	Cl	826, 822(sh)	308	—[a]	[b]
Cs	Cl	824, 814			2
Cs	Cl	818	325, 285	305	20
Cs	Cl	830	322	307	21
Rb	Cl	834	308	—	[b]
Rb	Cl	815	318, 281	301	20
Cs	Br	829, 824	230	—	[b]
Cs	Br	824	250, 218	309	20
Cs	Br	825, 821	230, 226(sh)	—	22
$[AsPh_4]$[c]	Br	814	248, 212	298	20

[a] No bands observed.

[b] This work.

[c] No preparative details reported.

analogues.[23] The salts reported here were all found to be diamagnetic.

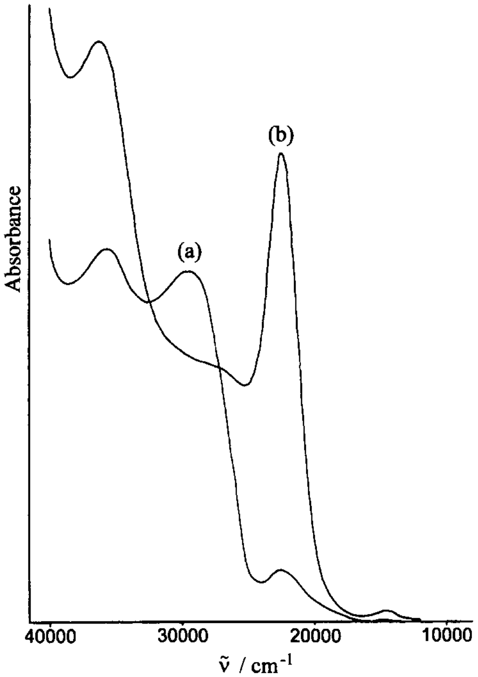


Fig. 1. The electronic absorption spectra of $Cs_2[RuO_2Cl_4]$ in 1 M hydrochloric acid 30 min (a) and 24 h (b) after dissolution.

The behaviour of $[RuO_2Cl_4]^{2-}$ *in water*

The instability of $[RuO_2Cl_4]^{2-}$ in water, in which it decomposes according to eq. (1), is long-established and empirically self-evident. The reactions and stability of $[RuO_2Cl_4]^{2-}$ in hydrochloric acid, in the presence or absence of dichlorine, are less well understood; there has only been one detailed study of $[RuO_2Cl_4]^{2-}$ in acidic media, published as an unclassified UKAEA report,[2] and this account contains many ambiguities. For example, Woodhead and Fletcher[2] found it necessary to stabilize solutions of $[RuO_2Cl_4]^{2-}$ in dilute hydrochloric acid by saturating the solvent with dichlorine, whereas Howe[1] reported that $Cs_2[RuO_2Cl_4]$ could be recrystallized unchanged from cold dilute hydrochloric acid. Figure 1 shows that in 1 M hydrochloric acid, the complex $[RuO_2Cl_4]^{2-}$ {or, more correctly, $[RuO_2Cl_{4-n}(H_2O)_n]^{(2-n)-}$ ($n = 0, 1$ or 2)} is reduced to a complex on the hydration chain from $[Ru_2OCl_{10}]^{4-}$, commonly referred to as Y2 (sometimes tentatively proposed as $[(H_2O)Cl_3Ru(\mu-O)_2RuCl_3(OH_2)]^{2-}$).[2,3,24] Ignoring the hydration phenomena, this reduction may be represented by eq. (5). The electronic spectrum of $Cs_2[RuO_2Cl_4]$

$$2[RuO_2Cl_4]^{2-} + 6[H_3O]^+ + 6Cl^- \longrightarrow [Ru_2OCl_{10}]^{4-} + 9H_2O + 2Cl_2 \quad (5)$$

was then recorded in 1 M hydrochloric acid saturated with dichlorine (which itself shows an intense absorption at *ca* 31,000 cm^{-1}). Despite considerable difficulty in obtaining a flat baseline (even small changes in the Cl_2 concentration in either the sample or reference beam leads to gross spectral distortion), and an effective solvent cut-off at *ca* 36,000 cm^{-1}, the spectrum of this solution is shown in Fig. 2; it showed no tendency to change with time. It is similar in profile to that reported by Woodhead and Fletcher[2] (see Table 2), and differences merely emphasize the problems in accurately

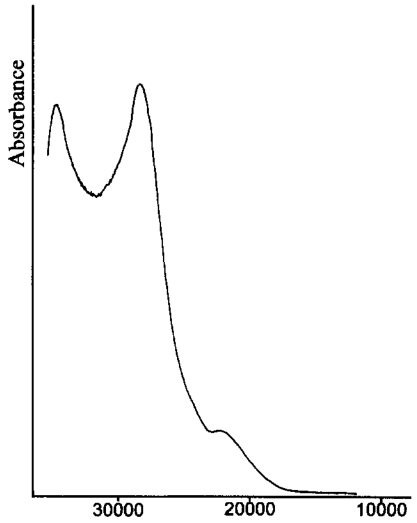


Fig. 2. The electronic absorption spectrum of $Cs_2[RuO_2Cl_4]$ in 1 M hydrochloric acid saturated with dichlorine.

Table 2. Electronic absorption spectral data for oxohaloruthenate(VI) salts

Salt	Solvent	$\tilde{\nu}_{max}$ (cm^{-1})[a]
$Cs_2[RuO_2Cl_4]$	1 M HCl	35,700 (5090), 29,700 (4800), 22,500 (710), 14,700 (25)[b]
	1 M HCl[c]	34,500 (3840), 28,200 (4320), 21,300 (165)
	3 M HCl[c,d]	33,300 (5500), 28,800 (7700), 20,800 (185)
$[AsPh_4][RuO_2Cl_3]$	ionic liquid[e]	—[f] 27,900 (6170), 20,500 (1540), 17,000 (590)

[a] Molar coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.
[b] Probably due to reduction product.
[c] Saturated with dichlorine.
[d] Data from ref. 2.
[e] Basic [*N*Bupy]Cl–$AlCl_3$ (44.44 mol% $AlCl_3$) ionic liquid.
[f] Beyond solvent cut-off.

correcting for the presence of Cl_2, whose absorbance maximum falls almost exactly halfway between the two strongest observed bands of the solute $[RuO_2Cl_{4-n}(H_2O)_n]^{(2-n)-}$. The effect of increasing the HCl concentration (in an attempt to suppress the hydration chain) was investigated, but the solution spectrum of $Cs_2[RuO_2Cl_4]$ in 12 M hydrochloric acid saturated with dichlorine was identical to that of $Cs_2[RuCl_6]$ in 12 M hydrochloric acid.[2,3] Thus, at higher hydrochloric acid concentrations, reaction (2) proceeds rapidly, even in the presence of an excess of dichlorine.

The behaviour of $[RuO_2Cl_4]^{2-}$ *in basic ionic liquid*

In an attempt to eliminate hydrolysis and hydration phenomena,[25] the electronic absorption spectrum of $Cs_2[RuO_2Cl_4]$ was recorded in a basic [*N*Bupy]Cl–$AlCl_3$ ionic liquid (44.44 mol% $AlCl_3$). The complex dissolved with difficulty and a spectrum recorded some 2 h after the start of the dissolution procedure showed that, despite the presence of a strong band at 27,800 cm^{-1}, attributable to $[RuO_2Cl_4]^{2-}$, some reduction to $[RuCl_6]^{2-}$ had occurred. This reduction proceeded to completion over a period of several days. Thus, a sample of the more soluble $[AsPh_4][RuO_2Cl_3]$ was prepared, which has been shown elsewhere[7] to associate with an excess of chloride in solution to form $[RuO_2Cl_4]^{2-}$. Upon dissolution in the basic (44.44 mol% $AlCl_3$) ionic liquid, a clear orange–red solution formed, and its electronic absorption spectrum (Fig. 3) represents the first genuine solution spectrum of pure $[RuO_2Cl_4]^{2-}$ to be reported. This spectrum changes slowly, at 20°C, with time (Fig. 4), with the bands attributable to $[RuO_2Cl_4]^{2-}$ disappearing and bands assignable to $[RuCl_6]^{2-}$ appearing. The presence of the isosbestic point at 25,600 cm^{-1} suggests that the reduction does not proceed via an intermediate complex, and the spec-

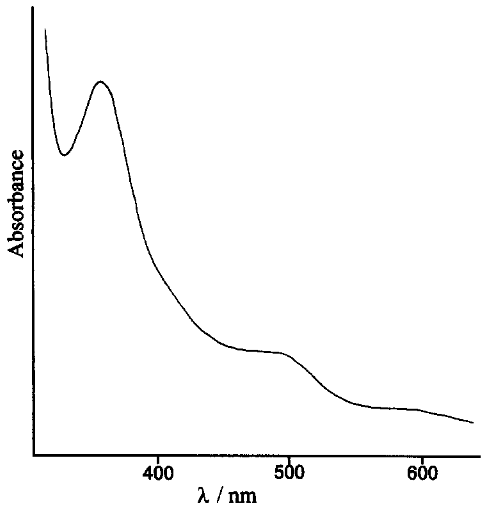


Fig. 3. The electronic absorption spectrum of $[RuO_2Cl_4]^{2-}$ (generated from $[AsPh_4][RuO_2Cl_3]$) in a basic $AlCl_3$–[*N*Bupy]Cl (44.44 mol% $AlCl_3$) ionic liquid, recorded immediately after dissolution.

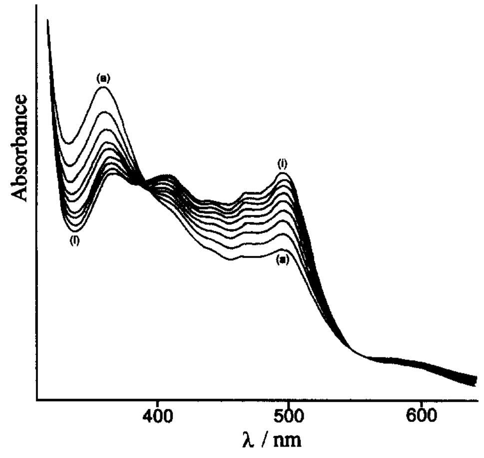


Fig. 4. The time dependence of the electronic absorption spectrum of $[AsPh_4][RuO_2Cl_3]$ in a basic $AlCl_3$–[*n*Bupy] Cl (44.44 mol% $AlCl_3$) ionic liquid. The spectra were recorded every 4 h from 7 h (a) to 39 h (i).

trum of the final product (Fig. 5) is essentially that of $[RuCl_6]^{2-}$, with a distortion present on the high energy edge of the main visible band (see below). This suggests that the most probable reaction to have occurred is given by eq. (6), a reaction formally analogous to eq. (2).

$$[RuO_2Cl_4]^{2-} + 2[AlCl_4]^- \longrightarrow [RuCl_6]^{2-} + 2\text{"}[AlOCl_2]^-\text{"} + Cl_2 \qquad (6)$$

A simple kinetic analysis of the data (Fig. 6) for the disappearance of the peak at 27,900 cm^{-1} gives a pseudo-first-order rate constant for the loss of $[RuO_2Cl_4]^{2-}$ of $k = (1.45 \pm 0.03) \times 10^{-5}\ s^{-1}$, whereas the rate constant for the formation of $[RuCl_6]^{2-}$ (as measured by the appearance of a peak at 20,200 cm^{-1}) was found to be $k' = (1.31 \pm 0.03) \times 10^{-5}\ s^{-1}$. This would suggest that about 10% of the ruthenium appears in a different complexed form, and the formation of a band at 24,700 cm^{-1} (which appears as a high energy distortion upon the form of the true $[RuCl_6]^{2-}$ spectrum[25]) is consistent with the formation of *ca* 5% of $[Ru_2OCl_{10}]^{4-}$ according to eq. (7), a reaction formally analogous to eq. (5).

$$2[RuO_2Cl_4]^{2-} + 3[AlCl_4]^- \longrightarrow [Ru_2OCl_{10}]^{4-} + 3\text{"}[AlOCl_2]^-\text{"} + 2Cl_2 \qquad (7)$$

$[Ru_2OCl_{10}]^{4-}$ shows a band at 27,100 cm^{-1} (with a shoulder at 26,000 cm^{-1}) in basic ionic liquids,[26] and at low concentrations this may well produce the observed spectral distortions; however, the identification of the by-product as $[Ru_2OCl_{10}]^{4-}$ must remain tentative.

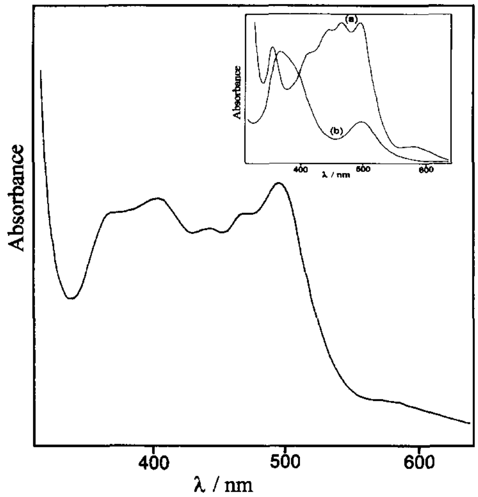


Fig. 5. The electronic absorption spectrum of $[AsPh_4][RuO_2Cl_3]$ in a basic [*N*Bupy]Cl–$AlCl_3$ (44.44 mol% $AlCl_3$) ionic liquid, recorded after 6 days, with inset spectra of $[RuCl_6]^{2-}$ (a) and $[Ru_2OCl_{10}]^{4-}$ (b) recorded in the same solvent.

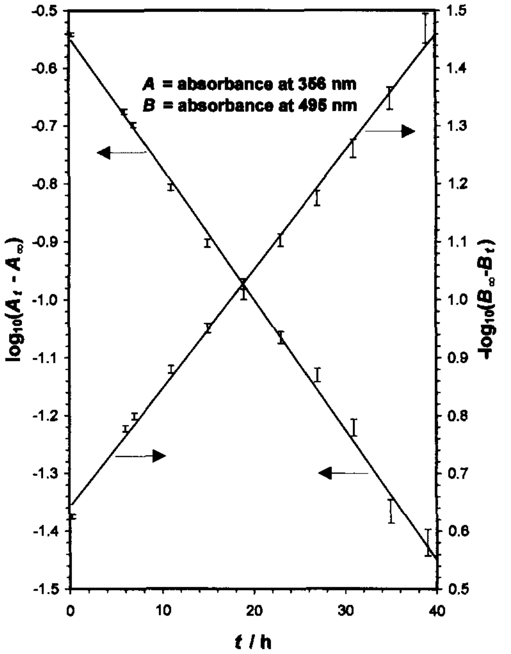


Fig. 6. Plots of $\log_{10}(A_t\text{-}A_\infty)$ against time for the absorbance at 356 nm (left-hand axis) and $-\log_{10}(B_\infty\text{-}B_t)$ against time for the absorbance at 495 nm (right-hand axis) for a solution of $[AsPh_4][RuO_2Cl_3]$ in a basic [*N* Bupy]Cl–$AlCl_3$ (44.44 mol% $AlCl_3$) ionic liquid at 20°C. The straight lines were each fitted to the experimental data by a conventional least-squares linear regression procedure, and represent a correlation coefficient of 0.996. The error bars were based upon an assumed constant error in absorbance of ±0.002.

Thus, it would appear that the behaviour of $[RuO_2Cl_4]^{2-}$ in aqueous hydrochloric acid and basic ionic liquids is formally similar, either $2[H_3O]^+$ or $[AlCl_4]^-$ acting as the oxide ion acceptors, respectively. Facile routes to both $[RuCl_6]^{2-}$ and $[Ru_2OCl_{10}]^{4-}$ are available, with high chloride ion concentrations favouring the formation of the former. The slower kinetics of reduction found in the ionic liquid facilitated the spectroscopic characterization of $[RuO_2Cl_4]^{2-}$. Reaction (6) is the first documented irreversible transfer of an oxide ion from an isolable transition metal complex to aluminium(III) in a room temperature ionic liquid.

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