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Vanadium chloride and chloride oxide complexes in an ambient-temperature ionic liquid. The first use of bis(trichloromethyl) carbonate as a substitute for phosgene in an inorganic system†

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The oxo exchange chemistry of vanadium chloride and chloride oxide complexes in solution in a room-temperature ionic liquid has been investigated, using a number of reagents. The structures of the solute species have been elucidated using a combination of electronic absorption spectroscopy and extended X-ray absorption fine structure. The reagent bis(trichloromethyl) carbonate has been used as a substitute for phosgene ($COCl_2$) in an inorganic system for the first time.

Ambient-temperature ionic liquids, based upon mixtures of 1-ethyl-3-methylimidazolium chloride [emim]Cl and aluminium chloride, have proven to be excellent solvents for spectrophotometric investigations of transition-metal chloride complexes.[1] In basic compositions, *i.e.* those with an excess of [emim]Cl, the absence of solvation and solvolysis reactions, combined with the ability to work at room temperature, leads to an environment in which these complexes may be stabilized. To date, little attention has been payed to complexes containing ligands other than chloride. The formation of metal oxochloro-complexes in ionic liquids containing oxide impurities, from hydrolysis with trace amounts of water, was noted and a titration procedure for the oxide level developed.[2] However, it was only with the introduction of a reliable method for the removal of oxide contamination, using phosgene ($COCl_2$), that the chemistry of these oxochloro-complexes has been investigated in any detail.[3,4]

Vanadium chlorides and chloride oxides are known in a number of oxidation states, and a wide range of salts have been isolated. The variety of oxovanadium groups that have been observed make vanadium-centred reactions a useful system to investigate this chemistry. In addition to performing oxygen-atom-transfer reactions,[5] vanadyl chloride complexes are known to undergo deoxochlorination reactions.[6] It has been shown that vanadyl species are stable in basic [emim]Cl–$AlCl_3$ ionic liquids.[7] This, together with the absence of the distortions usually associated with solvation and solvolysis interactions, makes [emim]Cl–$AlCl_3$ ionic liquids ideal solvents for the investigation of these complexes.

Although phosgene is an extremely effective reagent,[4,8] it is a toxic gas and extreme caution is required in its handling. Since the publication of an investigation by Eckert and Forster,[9] bis(trichloromethyl) carbonate, triphosgene, has become a popular substitute for phosgene in organic reactions. Triphosgene has been used for a wide range of reactions including chlorination, chloroformylation and dehydration processes.[9] It is a stable solid at room temperature, and may be handled using standard techniques for toxic solids. However, it is yet to be used in inorganic chemistry.

In this paper we introduce bis(trichloromethyl) carbonate as a substitute for phosgene in deoxochlorination reactions of metal chloride oxide complexes, and look at some oxidation reactions using both iodosylbenzene (PhIO) and dioxygen. We also investigate the structures of the vanadium chloride oxide complexes formed in a basic [emim]Cl–$AlCl_3$ ionic liquid, using extended X-ray absorption fine structure (EXAFS).

Experimental

Solvents and starting materials

Dichloromethane (BDH) and ethanenitrile (Aldrich) were distilled from phosphorus(v) oxide, under dry dinitrogen, immediately before use; thionyl chloride (Aldrich) and $VOCl_3$ (Aldrich) were distilled *in vacuo*, immediately prior to use. The salt [emim]Cl was prepared by the reaction of 1-methylimidazole with chloroethane.[10] The preparations of $[emim]_2[VOCl_4]$ and the [emim]Cl–$AlCl_3$ ionic liquids have been described elsewhere.[7,11] Iodosylbenzene was prepared by direct hydrolysis of iodobenzene.[12] Dioxygen and N_2 were dried by passage over a phosphorus(v) oxide column. Triphosgene (Aldrich) and VCl_3 (Aldrich) were used as supplied.

Preparations

$[emim]_2[VCl_6]$. Thionyl chloride (20 cm ^{3}) was added to $[emim]_2[VOCl_4]$ (1.22 g), forming a deep red solution. The solution was heated under reflux under dry dinitrogen for 2 h, to ensure complete reaction. The excess of $SOCl_2$ was removed *in vacuo*, leaving a red-brown residue. This solid was washed with aliquots (2 × 20 cm^{-3}) of dry dichloromethane. Finally the red-brown solid was dried *in vacuo*. Yield: 1.15 g (83.61%) (Found: C, 29.80; H, 4.70; N, 11.30. Calc. for $C_{12}H_{22}Cl_6N_4V$: C, 29.80; H, 4.60; N, 11.60%).

$[NEt_4][VO_2Cl_2]$. Sodium metavanadate (3.35 g, BDH) was added, with stirring, to a solution of 25% aqueous HCl. The salt $[NEt_4]Cl$ (4.60 g) was added to this yellow-orange solution. An orange precipitate began to form immediately. The mixture was stirred for 2 h to ensure complete reaction. The solid was isolated by vacuum filtration, washed with 25% aqueous HCl and placed in a desiccator, over anhydrous calcium chloride, overnight. The resulting red-brown solid was dissolved in hot ethanenitrile (100 cm^{-3}), under an atmosphere of dry N_2 to give a green solution. The volume of the solution was reduced until

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

precipitation began, and it was left to stand overnight. The resulting green precipitate was filtered off under N_2, and finally dried *in vacuo*. Yield: 5.07 (65%) (Found: C, 34.40; H, 7.30; N, 4.65. Calc. for $C_8H_{20}Cl_2NO_2V$: C, 33.90; H, 7.10; N, 4.95%).

Reactions in the basic ionic liquid

All reactions involving ionic liquids were performed using a combination of dry-box and Schlenk techniques. Product solutions were identified by their distinctive electronic absorption spectra (Fig. 1).[7,13]

$[VO_2Cl_2]^-$ with triphosgene. Triphosgene (0.026 g, 0.087 mmol) was added to a solution of $[NEt_4][VO_2Cl_2]$ (0.0075 g, 0.026 mmol) in a basic melt (3 cm^3). The yellow solution darkened through orange to brown. After stirring overnight the solution was degassed *in vacuo* for 2 h. The product solution was green.

$[VOCl_4]^{2-}$ with triphosgene. Triphosgene (0.575 g, 1.94 mmol) was added to a solution of $[emim]_2[VOCl_4]$ (0.1278 g, 0.296 mmol) in a basic melt (6 cm^3) and left to stir overnight. The red-brown solution was degassed *in vacuo* revealing a purple solution.

$[VCl_6]^{3-}$ with iodosylbenzene. Iodosylbenzene (0.10 g, 0.45 mmol) was added to a solution of VCl_3 (0.071 g, 0.45 mmol) in a basic melt (6 cm^3), and the mixture was stirred. The resultant solution was green.

$[VOCl_4]^{2-}$ with iodosylbenzene. Iodosylbenzene (1.15 g, 5.23 mmol) was added to a solution of $[emim]_2[VOCl_4]$ (0.0639 g, 1.48 mmol) in a basic melt (3 cm^3) and the mixture was stirred. The resultant solution was yellow.

$[VCl_6]^{3-}$ with O_2. Dry O_2 was bubbled through a solution of VCl_3 (0.047 g, 0.296 mmol) in a basic melt (6 cm^3) for 2 h. The resultant solution was green.

$[VCl_6]^{3-}$ and $[VO_2Cl_2]^-$. A solution of VCl_3 (0.0165 g, 0.105 mmol) in a basic melt (3 cm^3) was added to a solution of $[NEt_4][VO_2Cl_2]$ (0.030 g, 0.105 mmol) in a basic melt (3 cm^3) and stirred for 10 min. The resultant solution was green.

Spectroscopy

Infrared spectra were recorded on a Nicolet Magna 550 spectrometer, electronic absorption spectra on a Perkin-Elmer Lambda 2 spectrophotometer, using 1 cm pathlength cells.

Vanadium K-edge X-ray absorption spectra were recorded using the Synchrotron Radiation Source at the Daresbury Laboratory on Station 7.1 with an average beam current of 200 mA at 2 GeV. Harmonics were rejected from the Si(111) double-crystal monochromator by moving halfway down the rocking curve. Data for the solids $[emim]_2[VOCl_4]$ and $[NEt_4][VO_2Cl_2]$ were collected in transmission mode, with the samples being mixed with boron nitride such that an edge jump of *ca.* 1 was obtained. Solution data were acquired in the fluorescence mode using a single TlI/NaI scintillation counter. Samples were prepared in a dry nitrogen glove-box and sealed in Polythene bags, which were used as the sample cells. Only a very thin film of liquid was exposed to the beam to avoid problems with the 'thickness effect' due to the very high concentration of Cl in the samples.

For each sample, data used in the EXAFS fitting were the result of summing multiple runs. Analyses were performed in the EXCURV92 code, using spherical wave methods with *ab initio* phase shifts and backscattering factors, previously described elsewhere.[14] The solid compounds were used to obtain the proportion of the absorption affording EXAFS (0.7) and the magnitude of inelastic effects was modelled by an imaginary potential (−1.0 eV). The quality of the phase shifts can be checked by comparison with the metal–ligand distances which were within 0.01 Å of the available crystallographic data.[7,15]

Results and Discussion

Preparations

The salt $[emim]_2[VCl_6]$ was prepared by deoxochlorination of $[VOCl_4]^{2-}$, using $SOCl_2$.[6] Since it has been suggested[16] that $[VCl_6]^{2-}$ salts could be dissolved in, and recovered unchanged from, ethanenitrile, final purification by recrystallization from ethanenitrile was attempted. However, the material obtained was pale brown, rather than the expected dark red-brown, and its infrared spectrum clearly showed the presence of co-ordinated ethanenitrile (ν_{CN} 2296s and 2335m cm^{-1}). This result is, perhaps, less surprising when it is considered that co-ordination of ethanenitrile to vanadium centres is common. The ethanenitrile adducts $[VOCl_3(MeCN)]$[17] (oxidation state V), $[VOCl_2(MeCN)_x]$,[18] $[VCl_4(MeCN)]$[19] (oxidation state IV) and the salt $[AsPh_4][VCl_4(MeCN)_2]$[20] (oxidation state III) have all been characterized. Hence, the crude product was washed with dichloromethane, to avoid acetonitrile co-ordination.

The salt $[NEt_4][VO_2Cl_2]$ was prepared using an adaptation of the literature method,[21] which yielded an orange solid. The final green product was only obtained by recrystallization from dry ethanenitrile, and upon exposure to moisture in the air returned to orange. There was no evidence for the co-ordination of ethanenitrile to the vanadium.

Reactions in the basic ionic liquid

The results of the reactions in the ionic liquid are summarized in Table 1. A number of vanadium-containing compounds were dissolved in the basic ionic liquid. Whilst VCl_3, $[emim]_2[VOCl_4]$ and $[NEt_4][VO_2Cl_2]$ all gave the expected solute species when dissolved in a basic [emim]Cl–$AlCl_3$ ionic liquid, $[VCl_6]^{3-}$, $[VOCl_4]^{2-}$ and $[VO_2Cl_2]^-$ respectively, $VOCl_3$ and $[emim]_2[VCl_6]$ did not. On the basis of observations of other metal chlorides in ionic liquids, $VOCl_3$ would be expected to yield the $[VOCl_4]^-$ anion. However, the $[VOCl_4]^{2-}$ ion is formed in solution; this is not surprising since the tendency of $[VOCl_4]^-$ to reduce to $[VOCl_4]^{2-}$ in the presence of an excess of chloride ions is well known, and often leads to difficulty in the preparation of its salts. As with $[VOCl_4]^-$, $[VCl_6]^{2-}$ is spontaneously reduced in the basic melt, forming $[VCl_6]^{3-}$ in solution. Whilst, the room-temperature reduction of $[VCl_6]^{2-}$ salts to $[VCl_6]^{3-}$ has not been observed previously, thermal decomposition of $Cs_2[VCl_6]$ yields a product of oxidation state III, $Cs_2[VCl_5]$.[6] Also, VCl_4 itself is well known to be reduced by a range of donor molecules at room temperature.[22] It is likely that the large excess of chloride ion in the basic [emim]Cl–$AlCl_3$ ionic liquid leads to the reduction of the $[VCl_6]^{2-}$ ion.

With triphosgene. One major advantage of triphosgene over phosgene itself is that it may easily be used quantitatively. For example, when it is added to a solution of $[VO_2Cl_2]^-$ in the basic ionic liquid in a 1:3 ratio (each triphosgene molecule is equivalent to three molecules of $COCl_2$) a solution of $[VOCl_4]^{2-}$ is produced, but when added in excess a solution of $[VCl_6]^{3-}$ is generated.

Triphosgene, and indeed phosgene itself, is not a reducing agent and so the generation of $[VOCl_4]^{2-}$ (oxidation state IV) from $[VO_2Cl_2]^-$ (oxidation state V) and $[VCl_6]^{3-}$ (oxidation state III) from $[VOCl_4]^{2-}$ must be explained. In ethanenitrile treatment of $[VOCl_4]^{2-}$ with triphosgene yields $[VCl_6]^{2-}$. The ions $[VOCl_4]^-$ and $[VCl_6]^{2-}$ are unstable in the basic

Table 1 Summary of the experimental conditions and results for the transformations of the vanadium complexes

Ion	Solvent	Reagent	Proportion	Product
$[VOCl_4]^{2-}$	[emim]Cl–$AlCl_3$	Triphosgene	1 : 7	$[VCl_6]^{3-}$
	[emim]Cl–$AlCl_3$	$COCl_2$	Excess	$[VCl_6]^{3-}$
$[VO_2Cl_2]^-$	[emim]Cl–$AlCl_3$	Triphosgene	1 : 3	$[VOCl_4]^{2-}$
	[emim]Cl–$AlCl_3$	Triphosgene	Excess	$[VCl_6]^{3-}$
$[VCl_6]^{3-}$	[emim]Cl–$AlCl_3$	PhIO	1 : 1	$[VOCl_4]^{2-}$
$[VOCl_4]^{2-}$	[emim]Cl–$AlCl_3$	PhIO	1 : 4	$[VO_2Cl_2]^-$
$[VCl_6]^{3-}$	[emim]Cl–$AlCl_3$	O_2	Excess	$[VOCl_4]^{2-}$
$[VO_2Cl_2]^-$	[emim]Cl–$AlCl_3$	$[VCl_6]^{3-}$	1 : 1	$[VOCl_4]^{2-}$
$[VOCl_4]^{2-}$	MeCN	Triphosgene	Excess	$[VCl_6]^{2-}$
$[VO_2Cl_2]^-$	MeCN	Triphosgene	1 : 1	$[VOCl_4]^{2-}$

[emim]Cl–$AlCl_3$ ionic liquid (see above) and both are spontaneously reduced, yielding $[VOCl_4]^{2-}$ and $[VCl_6]^{3-}$ respectively. Hence these are the products formed.

In organic applications of triphosgene an amine base is added to the solution to catalyse its decomposition to phosgene.[2] In the reactions described here this was unnecessary, the chloride ion being sufficiently nucleophilic to serve this purpose.

Oxidation of vanadium species. Iodosylbenzene is an extremely effective oxygen-atom donor in these systems, oxidizing $[VCl_6]^{3-}$ to $[VOCl_4]^{2-}$ when used in a 1 : 1 ratio. As such it would be expected to lead to an increase of two in the oxidation number of the vanadium, from III to V. Indeed this was seen in the reaction of $[VCl_4(MeCN)_2]^-$ in ethanenitrile with PhIO to give mixtures of $[VOCl_4]^-$ and $[VO_2Cl_2]^-$.[5] However, the formation of $[VO_2Cl_2]^-$ is prevented by the comproportionation reaction of the product and the starting material (see below) and $[VOCl_4]^-$ is unstable in the basic ionic liquid, reducing to give $[VOCl_4]^{2-}$ in solution. It is, therefore, likely that the initial product of the reaction of PhIO and $[VCl_6]^{3-}$ in the basic ionic liquid is $[VOCl_4]^-$ which instantaneously reduces to $[VOCl_4]^{2-}$.

The use of an excess of PhIO with $[VOCl_4]^{2-}$, which would not be expected to act as a simple oxygen-atom acceptor since this would require the generation of a vanadium(VI) species, gives a solution of the $[VO_2Cl_2]^-$ ion. This is in good agreement with the reaction in ethanenitrile, which is accompanied by the production of chlorine gas.[5] No attempt was made to measure the production of Cl_2 here, but the reaction would be expected to follow a similar course.

When dry O_2 is bubbled through a solution of $[VCl_6]^{3-}$ in the basic ionic liquid, or Li_2CO_3 is added, a solution of $[VOCl_4]^{2-}$ is generated. Even on addition of a considerable excess no further reaction is observed.

Comproportionation of $[VCl_6]^{3-}$ and $[VO_2Cl_2]^-$. The mixing of solutions of the $[VCl_6]^{3-}$ and $[VO_2Cl_2]^-$ ions instantly gives a green solution of the $[VOCl_4]^{2-}$ ion. In a similar reaction of $[VO_2Cl_2]^-$ and $[VCl_4(MeCN)_2]^-$ in acetonitrile Zhang and Holm[5] proposed a solvated $[Cl_2V(O)\text{–}O\text{–}VCl_4]^{2-}$ intermediate. In the basic ionic liquid, where the solvent chemistry is dominated by the chloride ion and facile exchange of chloride ions between the solvent and solute complexes is expected, a solvated species is one that is co-ordinated by the maximum possible number of chloride ions. Hence, the reaction intermediate would be expected to be $[Cl_3V(O)\text{–}O\text{–}VCl_5]^{4-}$. This species would then undergo electron transfer and further chloride exchange to give the final product.

Spectroscopy

Infrared. The infrared spectra of the isolated salts were recorded as mulls in liquid paraffin and the V=O and V–Cl stretching frequencies are listed in Table 2. The spectra are sensitive to both the oxidation state of the vanadium and to the co-ordination geometry of the complex. The ion $[VO_2Cl_2]^-$ would be expected to show two V=O stretches (A_1 and B_1) and two V–Cl stretches (A_1 and B_2),[15] however the V–Cl stretches here are not resolved. For the simple octahedral complexes $[VCl_6]^{3-}$ and $[VCl_6]^{2-}$ group theory predicts just one V–Cl stretching frequency [ν_3, asymmetric (T_{1u}) stretch] seen at 304 and 353 cm^{-1}, respectively. This clearly indicates a strengthening of the V–Cl bond as the metal changes from oxidation state III to IV, however lack of crystallographic data precludes comparison with bond lengths for these complexes. The tetrachlorooxovanadate complexes $[VOCl_4]^{2-}$ and $[VOCl_4]^-$ both have tetragonal-pyramidal structures, and show a single V=O stretch (A_1 symmetry) and two V–Cl stretches (A_1 and E). Again a large increase in the V–Cl stretching frequencies is seen as the oxidation state increases from IV to V, with a smaller effect for the V=O stretching frequency. This is consistent with the available crystallographic data, and arises from the removal of an electron from an antibonding orbital of largely V–Cl character.[7] It can be seen that for the two complexes of oxidation state IV there is little change in the V–Cl stretching frequencies.

Table 2 Infrared spectral data for the vanadium complexes

Salt	$\tilde{\nu}$(V=O)/cm^{-1}	$\tilde{\nu}$(V–Cl)/cm^{-1}
$[Hpy]_3[VCl_6]$	—	304[23]
$[emim]_2[VCl_6]$	—	353
$[emim]_2[VOCl_4]$	1001	361 (asym.), 340 (sym.)[2]
$[VCl_2(15\text{-crown-}5)]$-$[VOCl_4]$*	1021	422 (sym.), 366 (asym.)[24]
$[NEt_4][VO_2Cl_2]$	995 (sym.), 946 (asym.)	437

* 15-crown-5 = 1,4,7,10,13-Pentaoxacyclopentadecane.

Electronic absorption. The spectra of $[VO_2Cl_2]^-$, $[VOCl_4]^{2-}$ and $[VCl_6]^{3-}$ were recorded in the basic ionic liquid (Fig. 1). The spectrum of $[VOCl_4]^{2-}$ has been discussed in detail elsewhere.[7] As a vanadium(V) species $[VO_2Cl_2]^-$ is d^0, and no d–d spectral bands are seen.

The spectrum of the $[VCl_6]^{3-}$ ion in the basic ionic liquid shows two distinct bands at 555.0 and 887.6 nm and a weak shoulder at *ca.* 450 nm (Fig. 1, Table 3). There are very few spectra of the $[VCl_6]^{3-}$ ion in the literature. The salts are difficult to prepare, and the ion reacts with most solvents that will dissolve the salts {*e.g.* in MeCN $[VCl_4(MeCN)_2]^-$ is formed}.[27] However, a room-temperature diffuse-reflectance spectrum of $[Hpy]_3[VCl_6]$ (py = pyridine) and high-temperature solution spectra in LiCl–KCl and [Hpy]Cl molten salts have been reported and are in good agreement with the results here (Table 3).[25,26] It is notable that the bands at 555.0 and 887.6 nm are considerably narrower than the equivalent bands in the high-temperature spectra, showing the impact of thermal-broadening effects.

For an octahedral d^2 complex three transitions (1)–(3) are predicted, which can be expressed in terms of the ligand-field parameter *Dq* and the Racah parameter *B*.[28] Using a graphical

Table 3 Electronic absorption spectral data for the $[VCl_6]^{3-}$ ion

System	λ_{max}/nm	λ_{max}/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}	Width at half height/cm^{-1}
[emim]Cl-$AlCl_3$	887.6	11 270	14.0	2 200
Room temperature	555.0	18 020	34.8	2 800
	450 (sh)	22 220		
LiCl-KCl	911	11 000	13.0	3 000
400 °C[26]	555	18 020	35.8	4 000
[Hpy]Cl	860	11 630	13.2	2 750
160 °C[26]	545	18 350	30.5	3 950
Solid	877	11 400		
Room temperature[25]	555	18 000		

$$\nu_1\ {}^3T_{2g} \longleftarrow {}^3T_{1g}$$
$$5Dq - 7.5B + 0.5(225B^2 + 100Dq^2 + 180DqB)^{\frac{1}{2}} \quad (1)$$

$$\nu_2\ {}^3A_{2g} \longleftarrow {}^3T_{1g}$$
$$15Dq - 7.5B + 0.5(225B^2 + 100Dq^2 + 180DqB)^{\frac{1}{2}} \quad (2)$$

$$\nu_3\ {}^3T_{1g}(P) \longleftarrow {}^3T_{1g}\,(225B^2 + 100Dq^2 + 180DqB)^{\frac{1}{2}} \quad (3)$$

approach,[27] Dq and B were calculated to be 1220 and 510 cm^{-1} respectively. This gives predicted energies of the transitions of 11 210 cm^{-1} for ν_1, corresponding to the band seen at 11 270 cm^{-1}, and 17 870 cm^{-1} for ν_3 corresponding to the band seen at 18 020 cm^{-1}. The energy of the ν_2 transition can also be calculated to be 23 410 cm^{-1}, which would give rise to a weak band at 427 nm. There is indeed a weak shoulder at *ca.* 450 nm (22 220 cm^{-1}) coinciding with the threshold of the charge-transfer band, which can be tentatively assigned to ν_2.

EXAFS. The vanadium K-edge EXAFS derived structural information for the solids $[NEt_4][VO_2Cl_2]$ and $[emim]_2[VOCl_4]$ and their solutions in the basic [emim]Cl-$AlCl_3$ ionic liquid is shown in Figs. 2 and 3 and is summarized in Table 4. The spectra were analysed with the proportion of absorption affording EXAFS set at 0.7 and the magnitude of the inelastic effects modelled by an imaginary potential (−1.00 eV). The spectra of both the solid and liquid samples were analysed using the summed raw data. Owing to the high background absorption of the liquid samples, caused by the high chloride concentration in the samples, the liquid data are somewhat poorer than that of the solid. Rather than treating these data for example by Fourier filtering, the summed raw data were used in the refinements.

The EXAFS-derived structural parameters for the solid $[emim]_2[VOCl_4]$ show good agreement with the crystallographic data, well within the error limits of the experiment (co-ordination number ±0.5, interatomic distance 0.01 Å),[7] confirming the choice of fitting parameters. The EXAFS of the solution formed when the salt is dissolved in the basic ionic liquid is in good agreement with the solid data. This indicates that, in the basic ionic liquids, the mean vanadium environments are largely the same as found in the solid state. In particular, there is no evidence for a chloride ion co-ordinating *trans* to the oxygen, which might have been expected since the formation of $[VOCl_5]^{3-}$ salts has been reported.[29] In addition to a substantial increase in the number of chloride ions in the co-ordination sphere, this would be seen as a lengthening of all the V–Cl bonds and particularly of the V=O bond. Additionally, a decrease in the wavenumber of the V=O stretch in the infrared spectrum would be expected and this is not seen.[7] There is no evidence for co-ordination of chloroaluminate species at the oxygen atom of the complex.

The EXAFS of solid $[NEt_4][VO_2Cl_2]$ is in good agreement with the available crystallographic data.[15] The mean V–O bond length as derived from the EXAFS spectrum of $[NEt_4][VO_2Cl_2]$ is slightly longer (1.61 Å) than that in $[PMePh_3][VO_2Cl_2]$ (1.581 Å). However, this difference is unlikely to be significant (errors for solutions: $r = \pm 0.03$ Å, $N = \pm 0.5$), and the V–Cl bond length is in very good agreement with the mean bond length in $[PMePh_3][VO_2Cl_2]$ of 2.225 Å.[15] Again there is good agreement between the EXAFS-derived structural parameters in solution and the solid state, indicating that there is no change in structure of the complex on dissolution in the ionic liquid. There is also no evidence for co-ordination of chloroaluminate species at the oxygen atoms, which would have presented itself as a lengthening of the V–O distance and the presence of an additional co-ordination shell.

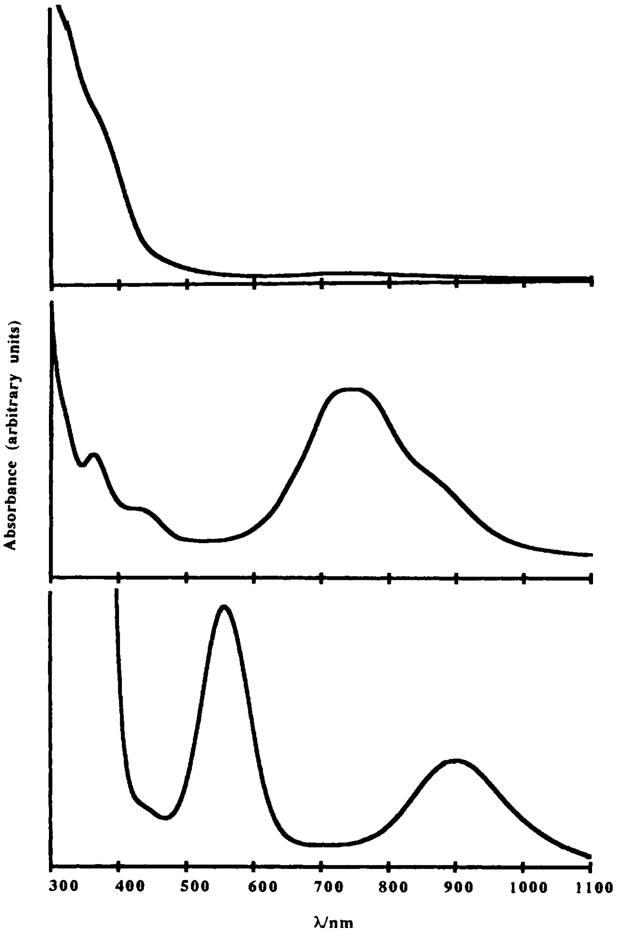

Fig. 1 Electronic absorption spectra of (top) $[NEt_4][VO_2Cl_2]$, (middle) $[emim]_2[VOCl_4]$ and (bottom) VCl_3 in a basic [emim]Cl–$AlCl_3$ ionic liquid

Conclusion

This study clearly indicates the utility of these ionic liquid systems for the investigation of the chemistry and spectroscopy

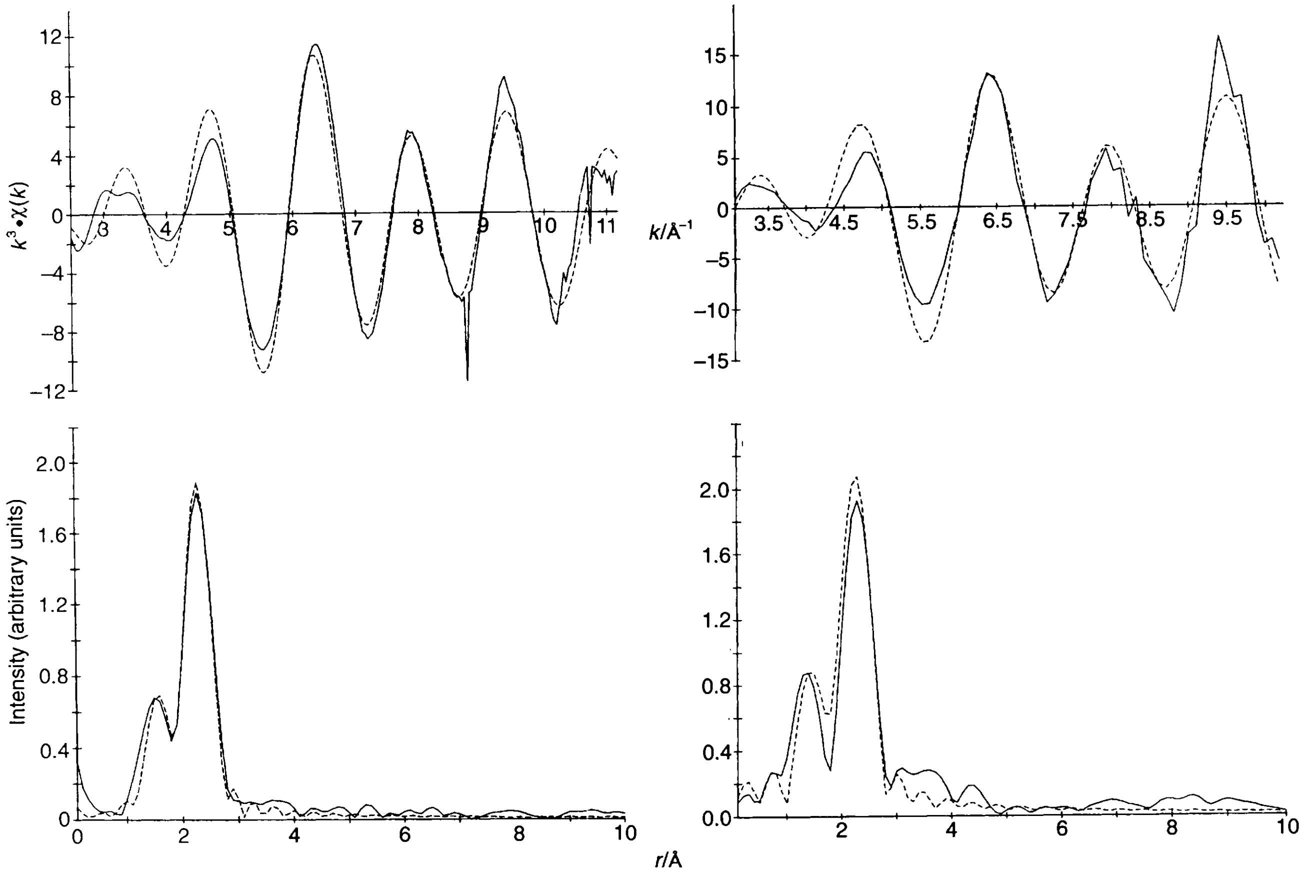

Fig. 2 Vanadium k^3-weighted EXAFS (top) and phase-corrected Fourier-transform moduli (bottom) of [emim]$_2$[VOCl$_4$] solid (left) and a solution of [emim]$_2$[VOCl$_4$] in basic ionic liquid (right). (– – –) Experimental data, (- - -) calculated curve

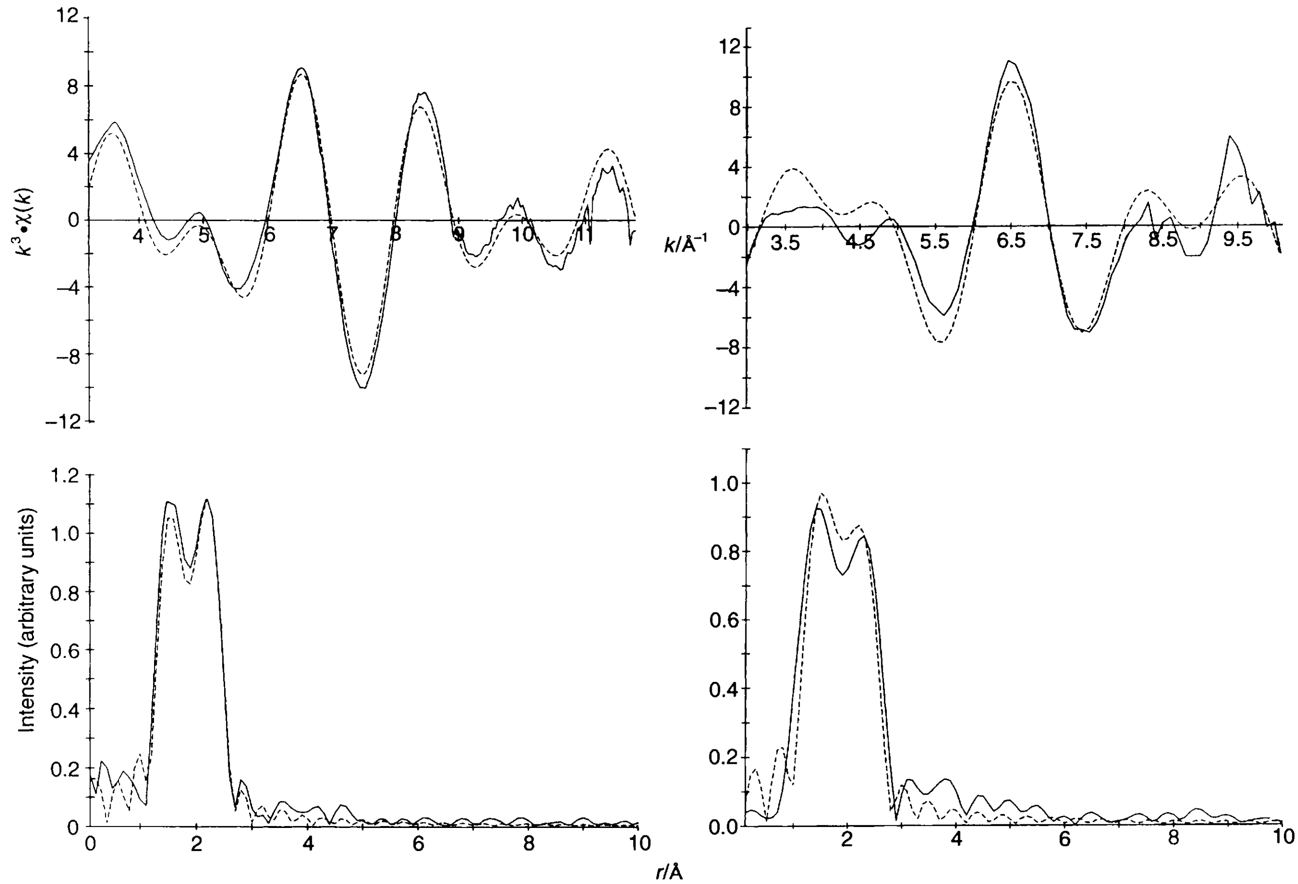

Fig. 3 Vanadium k^3-weighted EXAFS (top) and phase-corrected Fourier-transform moduli (bottom) of [NEt$_4$][VO$_2$Cl$_2$] solid (left) and a solution of [NEt$_4$][VO$_2$Cl$_2$] in basic ionic liquid (right). (– – –) Experimental data, (- - -) calculated curve

Table 4 The EXAFS-derived structural parameters for the vanadium complexes in the solid state and in the basic ionic liquid

Sample	N	r/Å	A/Å^2	R
$[emim]_2[VOCl_4]$ solid (transmission)	1.0 O	1.56	0.005	25.38
	4.0 Cl	2.32	0.010	
in basic ionic liquid	1.3 O	1.53	0.001	30.37
	4.0 Cl	2.31	0.006	
$[NEt_4][VO_2Cl_2]$ solid	2.0 O	1.61	0.004	24.79
	2.0 Cl	2.23	0.007	
in basic ionic liquid	2.0 O	1.57	0.005	43.36
	2.0 Cl	2.26	0.008	

N = Occupancy of co-ordination shell, r = vanadium–ligand distance, A = Debye–Waller factor, $2\sigma^2$.

of chloride oxide complexes as well as simple chloride complexes. It also demonstrates that the EXAFS technique can be successfully applied to complexes with lower symmetry than those previously investigated in the ionic liquids. We have demonstrated the use of triphosgene as a substitute for phosgene in deoxochlorination reactions of transition-metal complexes in both the ionic liquids and ethanenitrile solutions, and would recommend its use.

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