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Ionic liquids with trichloride anions for oxidative dissolution of metals and alloys†

Xiaohua Li, [iD] Arne Van den Bossche, Tom Vander Hoogerstraete [iD] and Koen Binnemans [iD] *

Ionic liquids (ILs) with trichloride anions ($[Cl_3]^-$) combined with different cations were synthesised by bringing chlorine gas into contact with the corresponding chloride (Cl^-) ILs at room temperature. These trichloride ILs safely store chlorine and are useful as oxidising agents for dissolution of various metals and alloys under mild conditions.

Dissolution of metals and alloys is an essential step for the recycling of metals from end-of-life products. Examples are recycling of gallium, indium and antimony from LEDs, samarium and cobalt from magnets, and gold from waste electrical and electronic equipment (WEEE). Traditional procedures for metal dissolution are pyrometallurgical and hydrometallurgical processes. Pyrometallurgy involves high-temperature processes which are often energy intensive. Hydrometallurgy is based on dissolving the metals in strong acids (*e.g.*, H_2SO_4 and HCl) or bases or involving microorganisms (bioleaching). However, this can lead to problems: formation of flammable or toxic gases and a large consumption of chemicals. In the case of dissolution of gold, conventional processes are based on aqueous solutions of cyanide salts or aqua regia, which are either toxic or highly corrosive.[1]

Alternatively, metals and alloys can be dissolved in organic solvents by first oxidising them with halogens to metal halides. Uranium, for example, has been dissolved in bromine–ethyl acetate mixtures.[2,3] Similar mixtures, *e.g.* bromine–methanol and chlorine–dimethylformamide, have been used for dissolving rhenium, zirconium, thorium, titanium and beryllium alloys, as well as acting as an etchant for semiconductors.[4–8] However, due to their high reactivity, halogens can attack the organic solvents and form halogenated by-products. Furthermore, the high

volatilities of halogens and organic solvents make them unattractive from an environmental point of view.

Ionic liquids (ILs) are solvents that consist entirely of ions.[9] They are often considered environmentally friendly alternatives for molecular solvents, because of their negligible vapor pressure. ILs can store halogens by forming trihalide or polyhalide anions, to be used as reagents for halogenation of organic compounds, such as aromatics, alkenes and alkynes.[10,11] Most reported trihalide ILs comprise the $[Br_3]^-$, $[I_3]^-$ or multihalide anions (*e.g.*, $[ClBr_2]^-$, $[BrCl_2]^-$ and $[BrI_2]^-$),[12–18] but to the best of our knowledge, no room temperature trichloride ILs have been reported yet, with the exception of a few trichloride solid salts.[19,20] Nevertheless, trichloride ILs (with the $[Cl_3]^-$ anion) are very promising, because in most cases they are much more reactive towards metals than tribromide and triiodide ILs. Moreover, the chemical stability of the trihalide ions in organic solvents follows the order $[Cl_3]^- > [Br_3]^- > [I_3]^-$, whereas the stability order is reversed in water.[21]

In this communication, we report on the synthesis and characterisation of trichloride ILs, and their applications for oxidative dissolution of metals and alloys.

Trichloride ILs were prepared by bubbling chlorine gas into the corresponding chloride ILs at room temperature in a flask protected from light, because we observed that the trichloride ILs were light-sensitive. Detailed information on the synthetic procedure is given in the ESI.† To form trichloride ILs, the molar ratio of chlorine to the chloride IL was controlled to 1:1, which was achieved by slowly bubbling chlorine at a constant flow rate (controlled by a chlorine-resistant flow meter) for a given time. The mass of the added chlorine was obtained by measuring the mass difference of the flask before and after bubbling chlorine through it. The excess of chlorine in the flask was removed with a nitrogen gas purge. A total of 12 chloride ILs with various cations were transformed into the corresponding trichloride ILs. The names and abbreviations of the trichloride ILs are shown in Table 1 and their cationic structures are given in Fig. 1.

All the trichloride ILs were liquid at room temperature, even though some of the starting chloride ILs were solids (see Table 1).

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404,
B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@kuleuven.be

Table 1 Names, abbreviations and some physicochemical properties of the studied trichloride ILs and aggregation state of the trichloride ILs and their corresponding chloride ILs at room temperature (RT)

No.	Name of trichloride ILs	Abbreviation	T_m $(T_g)^a$ (°C)	ρ at 25 °C (g cm^{-3})	η at 25 °C (mPa s)	Aggregation state of ILs (RT)	
						Chloride ILs	Trichloride ILs
1	Trihexyl(tetradecyl)phosphonium trichloride	[P$_{666,14}$][Cl$_3$]	—^{b}	0.9470	407	Liquid	Liquid
2	Tetrabutylphosphonium trichloride	[P$_{4444}$][Cl$_3$]	17	1.0399	231	Solid	Liquid
3	Tributyl(tetradecyl)phosphonium trichloride	[P$_{444,14}$][Cl$_3$]	6	0.9785	399	Solid	Liquid
4	1-Butylpyridinium trichloride	[BPy][Cl$_3$]	—	1.2234	61	Solid	Liquid
5	Methyltrioctylammonium trichloride	[N$_{1888}$][Cl$_3$]	(−57)	0.9615	1109	Liquid	Liquid
6	1-Butyl-1-methylpyrrolidinium trichloride	[BMPyrr][Cl$_3$]	—	1.1650	63	Solid	Liquid
7	1-Butyl-2-methylpyridinium trichloride	[2-MBPy][Cl$_3$]	—	1.2093	95	Solid	Liquid
8	1-Butyl-1-methylpiperidinium trichloride	[BMPip][Cl$_3$]	(−50)	1.1539	301	Solid	Liquid
9	1-Butyl-4-methylpyridinium trichloride	[4-MBPy][Cl$_3$]	11	1.1860	96	Solid	Liquid
10	1-Hexylpyridinium trichloride	[HPy][Cl$_3$]	—	1.1662	65	Solid	Liquid
11	1-Butyl-3-methylimidazolium trichloride	[Bmim][Cl$_3$]	T_m (T_g), ρ and η were not studied			Solid	Liquid
12	1-Decyl-3-methylimidazolium trichloride	[Dmim][Cl$_3$]	T_m (T_g), ρ and η were not studied			Liquid	Liquid

^{a} Glass transition temperatures are shown in parentheses. ^{b} No transition was detected in the trace of differential scanning calorimetry (DSC).
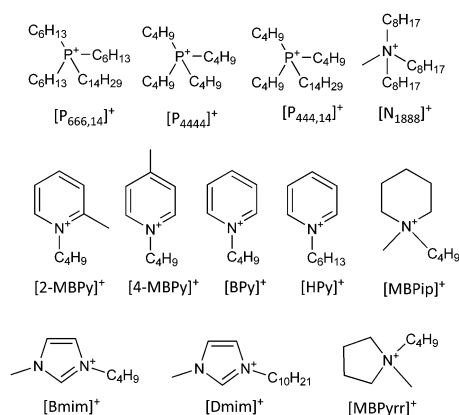
Fig. 1 Structures of the cations of the trichloride ILs described in the present study.

The formation of the [Cl$_3$]$^-$ ion proceeded very smoothly: yellow liquid drops were observed immediately after contacting the chlorine gas with the chloride ILs. The trichloride ILs were characterised by ^{1}H, ^{13}C, ^{31}P NMR to check the stability of the IL cation in the presence of chlorine gas. The results (Fig. S3 in ESI†) showed that the imidazolium cations were attacked by chlorine gas, because new peaks were observed in the ^{1}H NMR spectra of [Bmim][Cl$_3$] and [Dmim][Cl$_3$] when comparing their NMR spectra with those of [Bmim]Cl and [Dmim]Cl, respectively. Therefore, these are not further considered in this study. For all other trichloride ILs (no. 1–10 in Table 1), no changes in the NMR spectra were observed after transformation of the chloride into the trichloride ILs. ESI-MS spectra in the positive ionisation mode showed that the mass-to-charge ratios are in agreement with the cationic species in trichloride ILs (see ESI†). The results of elemental analysis are also in agreement with the calculated values for trichloride ILs (see ESI†).

The Raman spectra of the products no. 1–10 were then measured, because Raman spectroscopy is a very useful tool for the characterisation of polyhalide ions. Fig. S4 (ESI†) clearly shows a sharp peak at 274 cm^{-1} in the Raman spectrum of the trichloride IL [P$_{444,14}$][Cl$_3$], whereas no peak was observed in

that of the chloride IL [P$_{444,14}$]Cl. In each Raman spectrum of the 10 products, the sharp peak at 272–280 cm^{-1} was observed, which results from the symmetric stretching of the linear [Cl$_3$]$^-$ group (Fig. S5 in ESI†).[14,19] Peaks related to the stretching of the Cl$_2$ molecule (574 cm^{-1})[19] were not present in all trichloride ILs, indicating all the Cl$_2$ was chemically bound in a trichloride anion rather than simply dissolved in the IL.

We can hereby conclude that 10 trichloride ILs (no. 1–10 in Table 1) were successfully prepared without decomposing the cationic structures. These trichloride ILs could be stored in a closed vial in the fridge for several months without decomposition. However, chlorine was slowly released from the liquid, as evidenced by detection of small concentrations (around 1 ppm) of chlorine by the chlorine detector when the vials were opened. The vapour–liquid equilibrium of chlorine will be further studied.

The physicochemical properties of the trichloride ILs no. 1–10 were investigated, including their densities (ρ) and viscosities (η), melting points (T_m) and glass transition temperatures (T_g). The values of ρ and η at 25 °C, T_g and T_m are shown in Table 1 and ρ at other temperatures are presented in ESI.† Although all trichloride ILs are liquid at room temperature, some of them have a melting point above 5 °C, so solid trichloride ILs could be obtained below this temperature. The solid trichloride ILs are expected to be able to store chlorine gas more stably than the liquid form, which makes these trichloride ILs attractive for safe chlorine gas storage. All trichloride ILs have lower melting points than the corresponding chloride ILs, due to the increased charge delocalisation in the [Cl$_3$]$^-$ ion compared to the Cl$^-$ ion. Similarly, the viscosity of a trichloride IL is much lower than that of its corresponding chloride IL, because of the lower electrostatic attraction between the cation and the [Cl$_3$]$^-$ ion. For example, Fig. 2 shows that the viscosity of [P$_{666,14}$][Cl$_3$] at different temperatures is nearly 4 times smaller than that of [P$_{666,14}$]Cl (0.29 wt% water). Furthermore, the melting points, densities and viscosities of the trichloride ILs follow the same trend as those of the corresponding chloride ILs: ILs with longer alkyl chains have lower melting points, lower densities and higher viscosities. For example, the densities of the
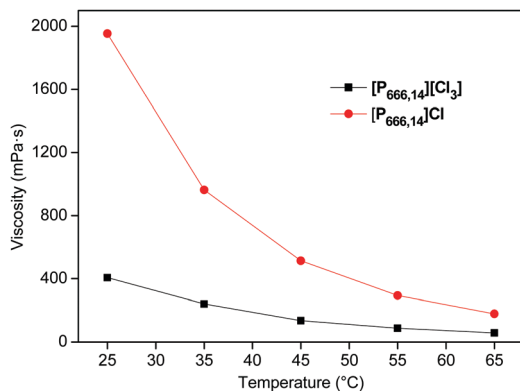
Fig. 2 Viscosities of $[P_{666,14}][Cl_3]$ and $[P_{666,14}]Cl$ as a function of temperature.

Fig. 3 Mixtures of metal chlorides and $[P_{444,14}][Cl_3]$ after complete dissolution of the corresponding metals and alloys.

three phosphonium trichloride ILs follow the order: $[P_{666,14}]$ < $[P_{444,14}]$ < $[P_{4444}]$. Fig. S6 (ESI†) shows that the densities all decrease linearly with increasing temperature.

The viscosities of the trichloride ILs were measured with a rolling-ball viscometer. However, it was observed that the used gold-coated stainless steel balls turned from gold-yellow to black after measuring the viscosity of trichloride ILs. This observation already suggested that the trichloride ILs are very reactive and that gold can be dissolved in trichloride ILs. This has been confirmed by a successful dissolution experiment of gold wire in a trichloride IL (see further). After dissolution of gold, the trichloride IL could further react with iron. All these reactions can cause the change of ball density and the smoothness of the ball surface while measuring, and hence lead to a measurement error. Therefore, the viscosity of one trichloride IL, $[P_{444,14}][Cl_3]$, was measured at 5 different temperatures with both a rolling-ball viscometer and a glass capillary Ubbelohde viscometer. The results (Fig. S7 in ESI†) show that the error of the rolling-ball viscometer was within 5% at 25, 30, 40 and 50 °C. However, the error reached 19% at 60 °C, implying the reaction rate increases with increasing temperature. Therefore, for the other trichloride ILs, only the viscosity at 25 °C was reported here with an error of 5%.

We selected $[P_{444,14}][Cl_3]$ as a representative trichloride IL for the study of the oxidative dissolution of metals. A total of 12 metals and 2 metal alloys were selected for dissolution tests: Fe, Cu, In, Zn, Ga, Sb, Au, Pt, Ge, Ta, Sm, Dy, GaAs and InAs. In a typical dissolution test, the metal (or alloy) was added to $[P_{444,14}][Cl_3]$ at a molar ratio of 1 : 8 in a 4 mL glass vial, after which the mixture was stirred by a magnetic stirring bar (10 × 6 mm) at 300 rpm at room temperature (25 ± 2 °C). The time needed for complete dissolution of the metal sample was recorded. Some of the metals were powders and others were small pieces. Additionally, the powders of different metals had different particle size which is an important parameter for the kinetics of metal dissolution. Therefore, one must be cautious when comparing the dissolution rates of the different metals and alloys. The particle size information of the employed metals and alloys is presented in Table S1 in ESI.†

Among the studied metals and alloys, 8 metals and 2 alloys shown in Fig. 3 could be completely dissolved in $[P_{444,14}][Cl_3]$ at
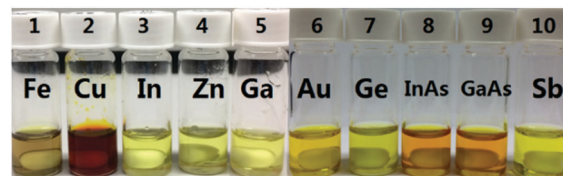
room temperature. Both Cu powder and Fe powder were completely dissolved in $[P_{444,14}][Cl_3]$ within 1 hour at a metal-to-IL molar ratio of 1 : 8. After complete dissolution, a second batch of Cu powder was added to vial 2 so that the total metal-to-IL molar ratio reached 1 : 5, which was dissolved again within 1 hour. Similarly, a second batch of Fe powder was added to vial 1 so that the metal-to-IL molar ratio was 1 : 4 and the extra added Fe powder dissolved completely within 3 hours. Vials 1 and 2 in Fig. 3 show the mixtures after complete dissolution of the second batch of powders, whereas the other vials have metal-to-IL molar ratio of 1 : 8.

Sb, Ge, In and Zn powders could be dissolved in $[P_{444,14}][Cl_3]$ within 3, 8, 20 and 28 hours at room temperature, respectively. Ga foil and Au wire dissolved relatively slowly and it took 46 and 30 hours respectively for complete dissolution. Pieces of InAs and GaAs showed full dissolution after 15 and 12 hours, respectively.

Extended X-ray absorption fine structure (EXAFS) spectra for Fe, Cu, Zn, Ga, In dissolved in $[P_{444,14}][Cl_3]$ were collected to obtain the geometry and the oxidation state of the metal complex after dissolution. The operational procedure and data fitting model are given in the ESI.† The EXAFS spectrum of the Fe-containing sample (Fig. 4) looks very similar to the one of $[FeCl_4]^-$.[22] In addition, the coordination number and the Fe–Cl bond lengths are in agreement with several crystal structures containing the $[FeCl_4]^-$ complex.[23] None of the Fourier transforms showed a second peak so that di- or oligomerisation of the Fe(III) complexes can be excluded. Similarly, the data of the other metal complexes, presented in Table 2, and their Fourier transforms (in ESI†) are in agreement with literature data.[24–27]

The dissolution of four other metals (Sm, Dy, Ta and Pt) was also studied. After mixing $[P_{444,14}][Cl_3]$ with Ta powders or a Pt
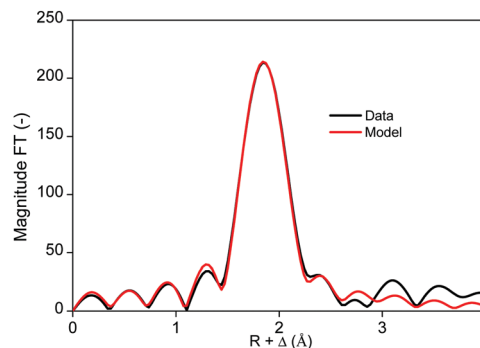

Fig. 4 Fourier transform of the EXAFS spectrum of the metal complex in trichloride ILs and fitted model of $[FeCl_4]^-$.

Table 2 Speciation results of the metal complexes after dissolution

Metal ion	Complex formed	N^a	R (Å)	Debye Waller (Å^2)
Fe(III)	$[FeCl_4]^-$	4.4(2)	2.208(2)	0.004(1)
Cu(II)	$[CuCl_4]^{2-}$	4.0(1)	2.244(1)	0.007(1)
Zn(II)	$[ZnCl_4]^{2-}$	3.9(1)	2.304(2)	0.006(1)
Ga(III)	$[GaCl_4]^-$	4.6(1)	2.184(1)	0.004(1)
In(III)	$[InCl_4]^-$	3.7(2)	2.365(3)	0.004(1)

^{a} Estimated standard errors are shown between parentheses.

wire for 35 hours, a large part of the solid material remained in the vials, showing that these metals did not dissolve well in the trichloride IL. The leachates were analysed by total reflection X-ray fluorescence (TXRF) and the results showed that Pt and Ta did not dissolve at all in trichloride ILs at room temperature. Sm and Dy pieces were mixed with $[P_{444,14}][Cl_3]$ for 26 hours at room temperature. We expected that Sm and Dy could easily be oxidised by $[P_{444,14}][Cl_3]$, due to the high reactivity of these rare-earth metals, but the TXRF results showed that only a very small amount of these metals was dissolved in the trichloride IL. After further mixing the samples at 50 °C for 24 hours, the TXRF results showed that the dissolved metal contents were still lower than 0.01 wt% on the basis of the original mass of the metal. This unexpected result (impossibility to dissolve Sm and Dy metals in the trichloride ILs) is very likely due to the presence of a passivating layer on the surface of the metals, preventing it from being attacked by the trichloride IL.

In conclusion, we have synthesised a series of trichloride ILs and these ILs performed well as solvents for oxidative dissolution of metals and alloys under mild conditions. Moreover, the trichloride ILs can selectively dissolve some metals while leaving other metals untouched. This is a useful property to achieve separation of mixtures of metals, for instance to separate the highly valuable metals Au and Pt. Further research on metal dissolution with these trichloride ILs is ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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