Rapid ligand substitution reactions in ionic liquids studied by stopped-flow technique†

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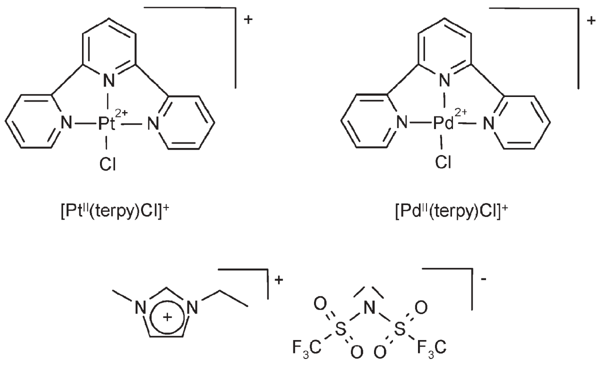
Detailed kinetic studies on ligand substitution reactions of $[M^{II}(terpy)Cl]^+$ complexes (M = Pt, Pd; terpy = 2,2′:6′,2″-terpyridine) with thiourea as entering nucleophile were for the first time performed in the imidazolium based ionic liquid [emim][NTf_2] using stopped-flow techniques, opening the route to study fast reactions of transition metal complexes in ionic liquids.

In recent years, ionic liquids have become a popular research area expected to grow even further as a result of potential industrial applications.[1,2] Such liquids are not only interesting in terms of applications in separation techniques,[3] but also because of the high solubility of gases that are insoluble in classical solvents.[4] Furthermore, in some cases such solvents increase the catalytic activity of reactions involving metal complexes.[5] In most cases it is still unclear why catalytic systems show improvements such as faster conversion or higher yields of envisaged products in ionic liquids.[6] In many cases reactions that are well understood in conventional solvents, are performed in ionic liquids although it is unclear if the catalytic active complex reacts according to the same mechanism as in conventional solvents. So far only a few mechanistic investigations have been undertaken in ionic liquids; some reported no change in the mechanism at all,[7] whereas others reported severe differences such as a complete changeover in mechanism on switching between two ionic liquids.[8–10] Most of the mechanistic investigations so far have been performed on slow inorganic[7] and organic[11,12] substitution reactions on a time scale of 15 min up to several hours.

It is our aim to study fast inorganic/bioinorganic reactions in ionic liquids on a subsecond time scale using stopped-flow methods in order to investigate the effect of ionic liquids on the rate and mechanism of important catalytic processes such as oxygen, superoxide, peroxide, nitric oxide and C–H activation. Such measurements will allow the determination of thermal and pressure activation parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta V^\ddagger$) that will in turn contribute to the elucidation of the underlying reaction mechanisms. We report here, as far as we know, the first stopped-flow measurements on rapid inorganic substitution reactions in ionic liquids.

We studied the reaction of $[Pt^{II}(terpy)Cl]^+$ (terpy = 2,2′:6′,2″-terpyridine) (see Scheme 1) with thiourea (TU) that was investigated in detail in various solvents before,[13] in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [emim][NTf_2]. This ionic liquid has suitable properties for the investigation of reaction kinetics (see Table 1). The viscosity is low compared to other ionic liquids and the optical pureness is very good even for studies in the UV range down to 250 nm (Fig. S1, ESI†).

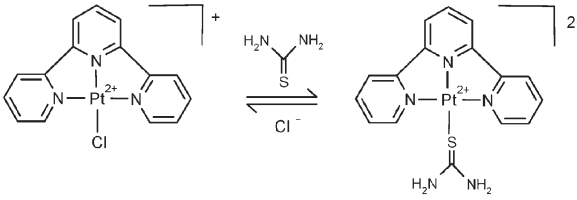


$[Pt^{II}(terpy)Cl]^+$ $[Pd^{II}(terpy)Cl]^+$

1-ethyl-3-methylimidazolium bis-trifluoromethylsulfonylamide, [emim][NTf_2][1]

Scheme 1

Due to its hydrophobic character, the solubility of [Pt(terpy)Cl]Cl and thiourea was limited to concentrations of about 0.4 and 80 mM, respectively, at room temperature, which was high enough for the investigation. The spectral changes that accompany reaction (1) are shown in Fig. S2 (ESI†).



(1)

The kinetic measurements were done under pseudo-first-order conditions (with thiourea in excess) at 360 nm and yielded good reproducible kinetic traces (see Fig. 1). A mixing time of about 20 ms due to the relative high viscosity of the ionic liquid was observed. Therefore, the first 20 ms were excluded from the

Table 1 Physical properties of [emim][NTf_2][1]

Viscosity, η (25 °C)/cP	Melting point, T_m/°C	Density, ρ (25 °C)/g ml^{-1}
34	−17	1.52

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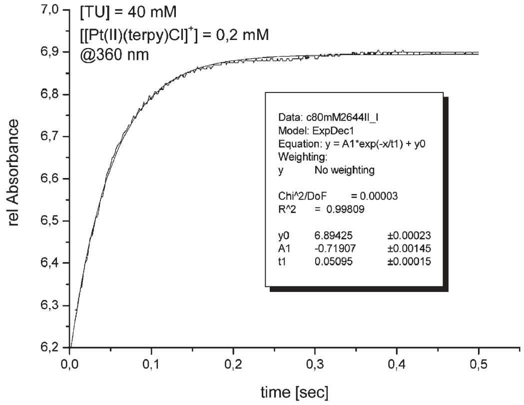


Fig. 1 Typical kinetic trace for reaction (1).

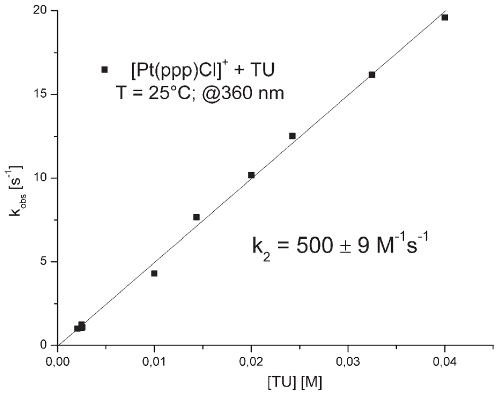


Fig. 2 Concentration dependence of reaction (1) at 25 °C.

Table 2 Rate and activation parameters for reaction (1) with thiourea in different solvents

Solvent	k_2 (25 °C)/M^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
[emim][NTf_2]	500 ± 9	32.0 ± 0.3	−88 ± 1
Water	2797 ± 42	29 ± 1	−82 ± 2
Methanol	1344 ± 21	35 ± 1	−67 ± 3

mathematical fit of the kinetic traces. The kinetic trace in Fig. 1 illustrates that the studied reaction is over in 0.2 s. The traces could all be fitted with a single exponential function under pseudo-first-order conditions. Values of k_{obs} were measured as a function of thiourea concentration for which the data is summarized in Fig. 2. Rate constants of up to 20 s^{-1} could be measured without any difficulties, *i.e.* a half-life of 35 ms. The slope of the line in Fig. 2 presents the second-order rate constant for the substitution of chloride by thiourea as expressed in reaction (1). The value of k_2 is compared with data from the literature[7] for other solvents in Table 2.

The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were determined from the temperature dependence of reaction (1) for which the Eyring plot is reported in Fig. 3 and summarized along with literature data in Table 2. The value of k_2 determined in the ionic liquid is about six times smaller than in water and about three times smaller than in methanol. The activation enthalpy and entropy do not show a specific trend as a function of the solvent, and the ionic liquid seems to behave as a conventional solvent. The fast reaction in water is accompanied by the lowest activation enthalpy, whereas the slowest reaction in [emim][NTf_2] is characterized by the most negative activation entropy. All the studied reactions show a significantly negative activation entropy in line with the associative nature of the ligand substitution process. The results clearly outline the innocence of the applied ionic liquid in terms of the mechanism of the studied substitution reaction. The only effect of performing the reaction in an ionic liquid seems to be a slight decrease in the reaction rate. This may be due to an interaction of the anionic component of the ionic liquid with the electrophilic metal centre, partially blocking the axial sites for associative nucleophilic attack by the entering ligand. This aspect is presently being investigated in more detail.

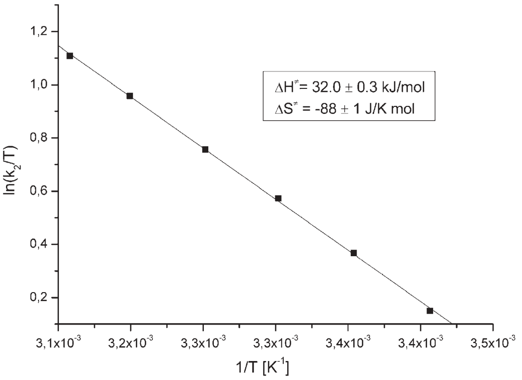
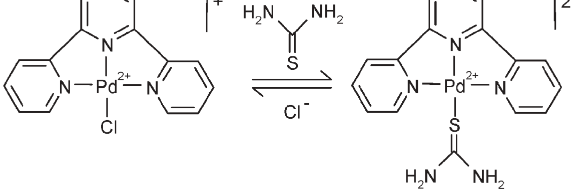


Fig. 3 Temperature dependence of k_2 for reaction (1).

Since most ionic liquids contain a significant concentration of dissolved water, it is important to know the water content and to determine whether it affects the investigated reaction. We observed a slight increase in the observed rate constant of reaction (1) on addition of small traces of water (Fig. S3, ESI†). This could be due to an increase in polarity of the solvent or a decrease in the viscosity of the ionic liquid. Because of this behaviour, all measurements were performed in the thoroughly dried ionic liquid with a water content of between 55 and 70 ppm as determined by Karl–Fischer titration.

To test the limits of the stopped-flow technique for the investigations of fast reactions in ionic liquids, we studied the same reaction but for the corresponding palladium complex as shown in reaction (2).



(2)

In general Pd(II) complexes are five to six orders of magnitude more labile than the corresponding Pt(II) complexes.[14] In water as solvent it was not possible to measure the kinetics of this reaction since it is too fast for the stopped-flow technique. However, in [emim][NTf_2] we were able to measure k_{obs} values of up to 129 ± 7 s^{-1} ([TU] = 4 mM) at 25 °C (see Fig. 4, the observed spectral changes that accompany the reaction are shown in Fig. S4, ESI†). Reactions at higher TU concentrations could not be measured

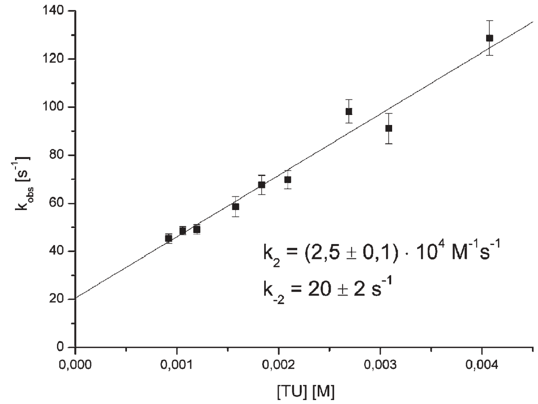


Fig. 4 Concentration dependence of reaction (2) at 25 °C.

Table 3 Comparison of the rate and activation parameters for reactions (1) and (2) in [emim][NTf$_2$]

Complex	k_2 (25 °C)/M^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
[Pt^{II}(terpy)Cl]$^+$	500 ± 9	32.0 ± 0.3	-88 ± 1
[Pd^{II}(terpy)Cl]$^+$	$(2.5 \pm 0.1) \times 10^4$	22 ± 2	-82 ± 6

because of the mixing time of 20 ms for this ionic liquid as solvent as mentioned above. The highest rate constant corresponds to a half-life of 5.4 ms, such that only the last 10% of the reaction can be observed following effective mixing of the reactants in the stopped-flow instrument. Fig. 4 exhibits a significant intercept which is ascribed to a reverse or parallel reaction for this very labile Pd(II) complex. As the water content of the ionic liquid is between 55 and 70 ppm, *i.e.* a water concentration of between 4.5 and 6 mM, this means that water is present in a 20 fold excess since the complex concentration was always kept at about 0.3 mM. For this reason we ascribe the intercept to a parallel rate-determining solvolysis reaction that is followed by a fast displacement of water by thiourea. The value of k_2 is 50 times larger for the Pd(II) than for the Pt(II) complex as shown in Table 3. This modest acceleration is not as large as that observed for amine ligated complexes, since in the case of the terpy complexes the π-acceptor property of the chelate causes a large increase in the electrophilicity of the metal centre such that the effect of the metal itself (Pt(II) *vs.* Pd(II)) diminishes.[15]

The temperature dependence of reaction (2) was studied for several thiourea concentrations in order to obtain the value of k_2 as a function of temperature for which the Eyring plot is given in Fig. 5. The determined activation parameters, included in Table 3, indicate that the increase in k_2 for the Pd(II) complex is mainly due to a decrease in the activation enthalpy, which in turn is due to the higher electrophilicity of the Pd(II) centre that accelerates the associative attack of thiourea.

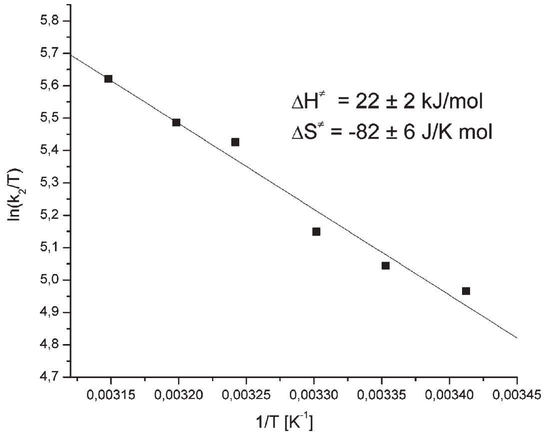


Fig. 5 Temperature dependence of k_2 for reaction (2).

The results obtained demonstrate clearly the possibility to perform detailed mechanistic investigations in the ionic liquid [emim][NTf$_2$]. The ionic liquid behaved like any common solvent and showed no further interaction with the studied Pt(II) and Pd(II) complexes. The activation parameters obtained in both cases point to an associative or associative interchange mechanism as expected for square planar coordinated Pt(II) and Pd(II) complexes. The water content of the ionic liquid seems to play a minor role in the case of the Pt(II) complex, but a bigger role in the case of the more labile Pd(II) complex, for which a parallel reaction was observed that could be related to the water content of the ionic liquid.

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