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Clustering of palladium(II) chloride in acetonitrile solution investigated by electrospray mass spectrometry

Vojtěch Šádek[a], Detlef Schröder[a,*], Nikos G. Tsierkezos[b]

[a] Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic
[b] Institut für Chemie, Elektrochemie und Galvanotechnik, Technische Universität Ilmenau, Weimarer Straße 25, 98693 Ilmenau, Germany

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ABSTRACT

Solutions of palladium chloride in acetonitrile are investigated by means of electrospray ionization mass spectrometry (ESI-MS). In contrast to several other metal salts previously investigated using ESI-MS, $PdCl_2$ has a pronounced tendency for aggregation to yield $[Pd_mCl_{2m-1}(CH_3CN)_n]^+$ clusters in the positive ion mode and $[Pd_mCl_{2m+1}]^-$ clusters when the negative ions are sampled, respectively. The observation of these oligomers parallels polymeric structures of $PdCl_2$ in the solid phase. The positive ions are most abundant for $m = 2$ and generally associated with several molecules of the solvent, whereas many different cluster sizes occur for the anions which generally do not appear as solvent associates. Parallel conductivity measurements in the condensed phase lend support to a pronounced tendency for aggregation of $PdCl_2$ in acetonitrile solution.

1. Introduction

Homogeneous palladium-containing catalysts are used in various chemical transformations [1–4]. Particularly C–C coupling reactions catalyzed by palladium catalysts, such as the Heck, Sonogashira, Suzuki, or Stille reactions, are of high importance in organic synthesis [5–7]. The formation of appropriate precatalysts with suitable ligands (phosphines, N-heterocarbenes, etc.) is generally achieved in situ using a simple salt like $PdCl_2$ as the metal-containing precursor. In the recent literature there is an increasing amount of examples that palladium catalysis proceeds via the formation of oligonuclear palladium species [8–10], casting some doubt on the so far frequent assumption that palladium catalysis involves discrete mononuclear entities. Solid palladium chloride can exist in distinct polymorphic structures. The polymeric α-palladium chloride consists of infinite chains of $Pd(\mu\text{-}Cl)_2$ units [11,12]. This form is barely soluble, thus it is often replaced in organic synthesis by the corresponding acetonitrile complex $PdCl_2(CH_3CN)_2$, which dissolves in organic solvents quickly and quantitatively. Solutions of $PdCl_2$ in acetonitrile have been studied by UV–vis spectroscopy [13]. The positions of the maxima in these spectra have been assigned to $PdCl_4{}^{2-}$ and $Pd_2Cl_6{}^{2-}$, respectively. The formation of $Pd_2Cl_{6+n}{}^{(2+n)-}$ species is triggered upon addition of LiCl [14]. β-Palladium chloride as another polymorph has a structure made from $[Pd_6Cl_{12}]$ cages [15] and is soluble in aromatic solvents [16].

In a dipolar solvent like acetonitrile, a metal(II) chloride MCl_2 can generally be expected to be involved in a series of dissociation and association reactions. Heterolysis leads in two steps from the neutral metal(II) halide via a metal-chloride cation to the corresponding dication, all of which are solvated (reactions (1) and (2)). The chloride ion released in both reactions may in turn add to the neutral precursor to form mono- or dianions (reactions (3) and (4)).

$$MCl_2 \rightarrow MCl^+ + Cl^- \quad (1)$$

$$MCl^+ \rightarrow M^{2+} + Cl^- \quad (2)$$

$$MCl_2 + Cl^- \rightarrow MCl_3{}^- \quad (3)$$

$$MCl_3{}^- + Cl^- \rightarrow MCl_4{}^{2-} \quad (4)$$

When the concentration of the metal salt is sufficiently high, the species formed in the primary reactions (1)–(4) can undergo further association reactions to form metal-chloride clusters. For example, the dinuclear monocation $[M_2Cl_3]^+$ can be formed via association of a monocation with a neutral metal species (reaction (5)) or of a dication with an anion (reaction (6)).

$$MCl^+ + MCl_2 \rightarrow [M_2Cl_3]^+ \quad (5)$$

$$M^{2+} + MCl_3{}^- \rightarrow [M_2Cl_3]^+ \quad (6)$$

Similar reactions can lead to the corresponding anionic species as well as to larger oligomers. Inspired by obvious correlations between ESI mass spectra and equilibria in solution [17], we

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* Corresponding author. Tel.: +420 220 463 117; fax: +420 220 462 583.
E-mail address: schroeder@uochb.cas.cz (D. Schröder).

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have recently initiated a research program aimed to probe such electrolyte equilibria by means of electrospray ionization mass spectrometry (ESI-MS). In general, it is assumed that electrospray ionization itself does not generate new ions, but it simply samples the ions either present as such in solution or formed via microscopic fluctuations, which are subsequently desolvated and transferred to the gas phase. Important to realize is that in ESI no 'hard' ionization event is applied as, for example, in classical electron ionization. Therefore, the molecular species present in solution are typically transferred to the gas phase as molecular or quasi-molecular ions [18]. Depending on the ionization conditions as well as the ions' stabilities, the initial species can pass unchanged to the mass spectrometer or can undergo further fragmentations [19–22]. Starting from first promising qualitative agreements [23–28], we meanwhile also achieved quantitative comparisons in selected cases [27,29–31]. Due to the frequent use of $PdCl_2$ solutions in acetonitrile in various synthetic procedures, here we accordingly report an ESI-MS study of this particular system.

2. Experimental details

The mass spectrometric measurements were performed with a Finnigan LCQ Classic ion-trap mass spectrometer (IT-MS) [32] by ESI of dilute solutions of $PdCl_2$ or $PdCl_2(CH_3CN)_2$ in acetonitrile. In brief, the LCQ bears a conventional ESI source (typical flow rate $5\,\mu l\,min^{-1}$, typical spray voltage 5 kV) with nitrogen as a sheath gas, followed by a heated transfer capillary (kept at 200 °C), a first set of lenses which determines the soft- or hardness of ionization by variation of the degree of collisional activation in the medium pressure regime [19–22], two transfer octopoles, and a Paul ion-trap with ca. 10^{-3} mbar helium for ion storage and manipulation, including a variety of MS^n experiments [33]. For detection, the ions are ejected from the trap to an electron multiplier. Due to the complex isotope patterns of higher palladium-chloride clusters in conjunction with the limited mass resolution of IT-MS, isobaric overlaps between ions of different stoichiometries occurring in several cases require modeling of the measured isotope pattern ion for the assignment of ion stoichiometries [24,34]. The abundances of the various palladium-containing clusters given in the diagrams below refer to the integrated isotope envelopes after correction for the baseline as well as signals of the pure solvent. Low-energy CID was performed by application of an excitation AC voltage to the end caps of the ion trap to induce collisions of the mass-selected ions with the helium buffer gas for a period of 20 ms at a trapping parameter of $q_z = 0.25$ [35–37]. For all mass spectra 200 scans were averaged with the XCalibur software.

Complementary conductivity measurements were carried out with a digital bridge-type conductivity meter (Metrohm 712). A conductance cell with electrodes of platinum black was used. The electrode was cleaned first with nitric acid solution, then with distilled water, and finally was dried with acetone. The cell constant was determined by measuring aqueous solutions of potassium chloride in the concentration range 1–100 mM [38]. The cell was kept at 21 °C using a water bath and the temperature was controlled with a digital thermometer. Throughout the measurements an atmosphere of argon was maintained over the solutions. The use of argon and a completely closed system resulted in conductance values with accuracy better than 0.2%. All measurements were performed twice for each concentration in order to probe the reproducibility. The raw conductivity data were corrected with the specific conductivity of acetonitrile as detailed elsewhere [39]. With regard to the analysis of the results, we refer to literature reports for other 2:1 unsymmetrical electrolytes in acetonitrile. According to Diamond et al. [40], the association constants of metal(II) perchlorates related to the second association step $MX^+ + X^- = MX_2$ (where M = metal ion and $X = ClO_4$), which is connected to the formation of neutral species, are negligible. Consequently, for studying the ionic association of metal(II) perchlorates in acetonitrile, the equilibrium for the first step association $M^{2+} + X^- = MX^+$, was considered to be sufficient to describe the experimental conductivity data. For $Mg(ClO_4)_2$ and $Ni(ClO_4)_2$ in acetonitrile at 25 °C, Kalugin et al. [41] reported association constants of $K_A = 282\,M^{-1}$ and $K_A = 162\,M^{-1}$, respectively. In contrast to metal(II) perchlorates, in the present studies the equilibrium constant of $PdCl_2$ related to the first step association $Pd^{2+} + Cl^- = PdCl^+$ was found to be more significant ($K_A \approx 3000 \pm 100\,M^{-1}$) and much greater than that determined for the second association step ($K_A = 664 \pm 40\,M^{-1}$). This finding indicates that ion association is favorable for $PdCl_2$ and thus the Pd-ions, which prevail in solution, are either the monocation $PdCl^+$ or the neutral $PdCl_2$–ion pairs. The first step association constant of $PdCl_2$ seems to be approximately one order of magnitude larger than those of $Ni(ClO_4)_2$ and $Mg(ClO_4)_2$, demonstrating that without any doubt the aggregation of $PdCl_2$ in acetonitrile is more significant compared to metal(II) perchlorates. However, some significant discrepancies between the published K_A values are obvious, which can be mainly attributed to the different models and approximations used for the determination of the association constants. For example, Libus and Strzelecki [42] reported an association constant of $K_A = 42\,M^{-1}$ for $Ni(ClO_4)_2$, which is much smaller than $K_A = 162\,M^{-1}$ obtained by Kalugin et al. under the same conditions [41]. We tried to achieve additional insight by variation of the chloride concentration. However, the additives used (i.e., KCl and tetrabutylammonium chloride) had themselves much larger conductivities than the (obviously mostly aggregated) $PdCl_2$ and this approach therefore was not practical. We note in passing that in ESI the addition of such external salts is even more devastating because their corresponding cations (i.e., $K(CH_3CN)_n{}^+$ and Bu_4N^+) comprise almost the complete ion current. For the time being, we are therefore left with the conclusion that the condensed-phase data indicate a pronounced association in the case of $PdCl_2$/acetonitrile, while an exact quantification is not a trivial task.

Palladium dichloride, bis(acetonitrile)-palladium chloride, and HPLC-grade acetonitrile were obtained from Sigma–Aldrich. Polymeric palladium chloride dissolves very slowly and the quantitative dissolution of a 1 mM sample takes about three days. Instead, $[PdCl_2(CH_3CN)_2]$ can be dissolved within minutes and the resulting mass spectra are identical within the experimental uncertainty. Stock solutions (3 mM) were prepared by accurate weighting of palladium salt and mixing with a measured volume of acetonitrile. These solutions were diluted to desired concentration. The uncertainty of the sample concentration is negligible compared to noise level and the concentration range, in which were these distinct samples measured. Due to memory effects, prior to measurements of concentration series, the inlet system was first carefully cleaned with pure solvent, and then the samples be measured in the sequence from the lowest to the highest concentration. Further, the solutions were tested for stability at upon storage at ambient room temperature in a dry, dark place. Spectra recorded after one week, one month, and after three months were identical within the experimental error.

3. Results and discussion

At the outset we note that the ESI mass spectra of $PdCl_2$ solutions in acetonitrile are much poorer in absolute ion abundances than the typical ESI mass spectra of metal(II) chlorides in protic solvents [22,28,43] and also than the ESI mass spectra of palladium(0) or palladium(II) complexes with larger organic ligands [44]. This general observation may be regarded as an indication that the heterolysis of $PdCl_2$ solutions in acetonitrile according to reaction (1)

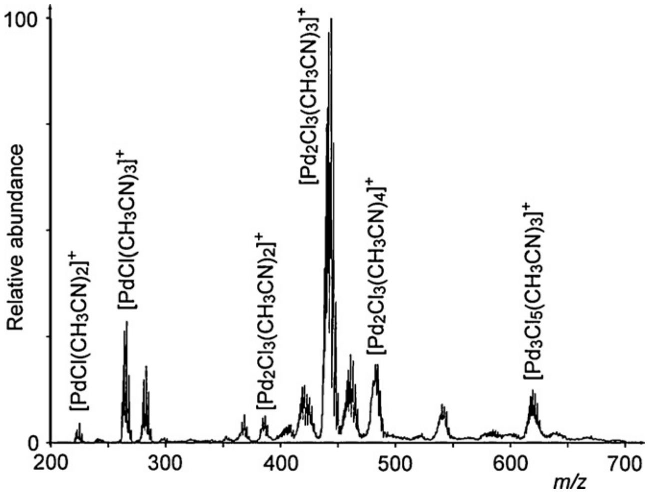

Fig. 1. Typical positive-mode ESI mass spectrum of $PdCl_2$ in acetonitrile.

is poor and/or that palladium chloride shows a large tendency for aggregation to clusters in acetonitrile solution.

3.1. Positive ions

At first, suitable ionization conditions for $PdCl_2$ solutions in acetonitrile had to be determined. To this end, a 10^{-4} M solution was measured at different settings of the capillary voltage (U_c), which determines the degree of multicollisional heating in the ion transfer zone between the ESI source operating at 1 bar and the vacuum manifold of the mass spectrometer [19–22]. All other parameters were adjusted to achieve maximal total ion count.

At soft conditions ($U_c = -10$ V), the spectrum is dominated by binuclear palladium clusters $[Pd_2Cl_3(CH_3CN)_n]^+$ with two or three acetonitrile ligands (Fig. 1). With increasing capillary voltage, the total ion count decreases, while the cluster ions undergo cleavage as well as reduction to Pd^I species due to collisional activation in the sampling interface to the mass spectrometer. At capillary voltages above $U_c > 50$ V, the spectrum is dominated by $[Pd(CH_3CN)_n]^+$ ions (Fig. 2). Accordingly, we have chosen $U_c = -10$ V as the optimal setting to sample the ions emerging from the solution with minimized fragmentation.

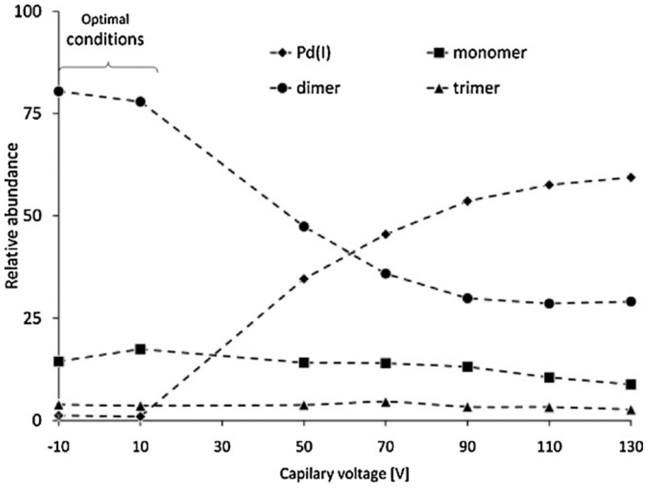

Fig. 2. Influence of capillary voltage U_c on the distribution of mono-, di-, and trinuclear Pd^{II} species $[Pd_mCl_{2m-1}(CH_3CN)_n]^+$ as well as the Pd^I cations $[Pd(CH_3CN)_n]^+$. The solid lines connecting the data points just serve to guide the eyes.

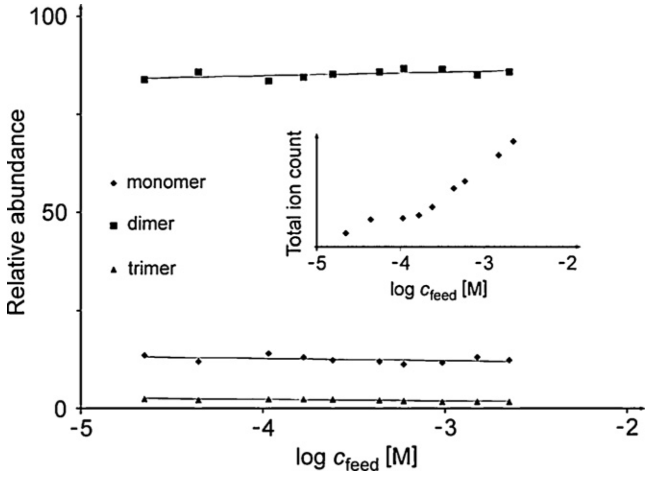

Fig. 3. Concentration dependence of the normalized abundances of the mono-, di-, and trinuclear species $[Pd_mCl_{2m-1}(CH_3CN)_n]^+$. The solid lines just serve to guide the eyes.

The dependence of cluster abundances on the sample concentration was measured up to concentrations of 3 mM; more concentrated solutions block the capillary and heavily contaminate the ion source. Spectra down to 10^{-7} M contained the desired peaks, but the level of noise was large. Accordingly, the results obtained with concentrations below 10^{-5} M were not evaluated quantitatively. As shown in Fig. 3, the abundances of monomeric and dimeric clusters are more or less independent from the concentration of the solutions admitted to the ESI probe (c_{feed}), whereas the total ion current shows the expected increase (see inset in Fig. 3). This observation does not fit with the intuitive expectation that the formation of larger aggregates, i.e., dinuclear clusters, should increase an elevated concentration of the monomeric precursor.

3.2. Negative ions

As chloropalladates are well-known species in the condensed phase, we expected also the formation of anionic species according to reactions (3) and (4). In addition to the mononuclear trichloropalladate anion $PdCl_3^-$, the negative-mode ESI mass spectrum (Fig. 4) contains a series of distinct $[Pd_mCl_{2m+1}]^-$ cluster anions with measurable abundances up to a cluster size of $m = 11$

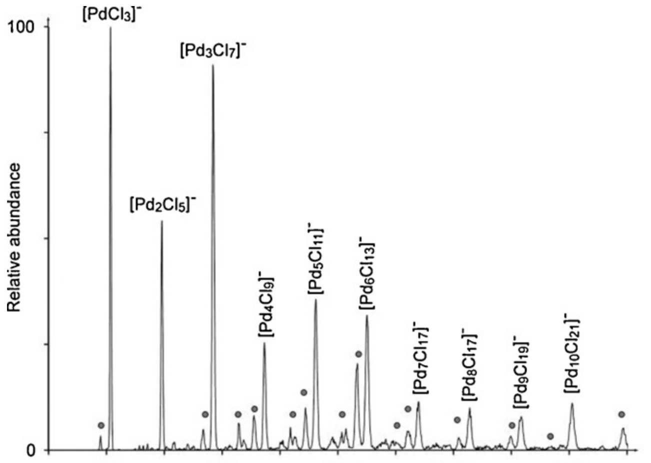

Fig. 4. Typical negative-mode ESI mass spectrum of $PdCl_2$ in acetonitrile. The grey dots indicate the reduced clusters containing formal palladium(I).

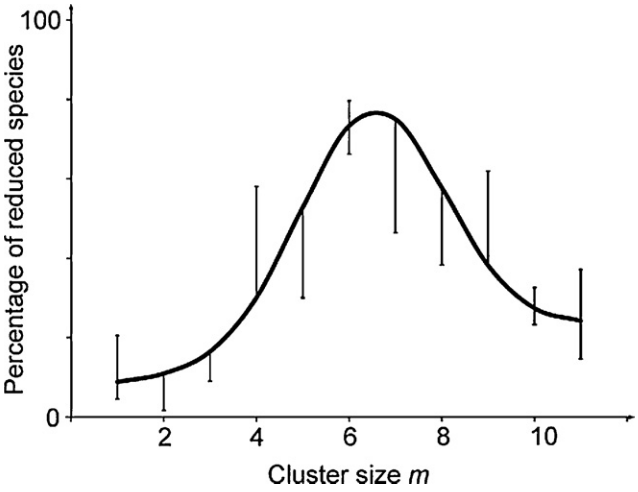

Fig. 5. Fraction of partial reduced $[Pd_mCl_{2m}]^-$ anions for each cluster size m; the entries represent the most probable value evaluated from multiple independent measurements.

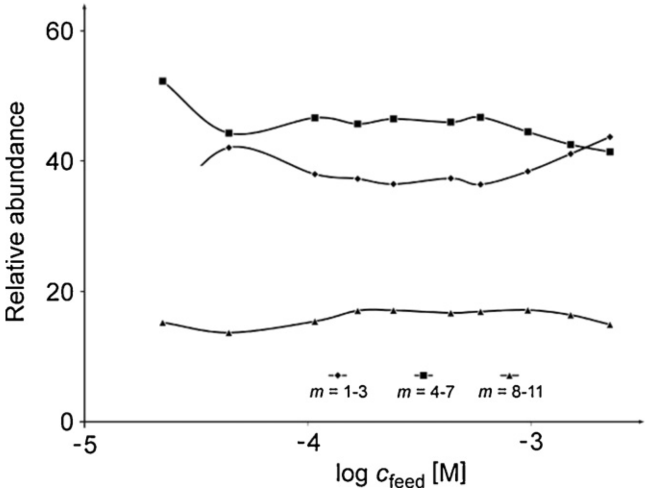

Fig. 7. Concentration dependence of the normalized abundances of the $[Pd_mCl_{2m+o}]^-$ anions (m = 1–11, o = 0, 1) for various cluster sizes. For the sake of visibility, the results are shown in groups for small (m = 1–3), medium (m = 4–7) and large (m = 8–11) clusters. The solid lines connecting the data points just serve to guide the eyes.

which is close to the upper mass limit of the instrument used (2000 amu).

A notable difference in comparison to the positive mode ESI spectra is that none of the anions is found to be associated with solvent molecules, which can be accounted for by the electronic properties of acetonitrile, which can serve as a donor for cations but is poor in stabilizing anions due to the lack of polar X–H bonds (X = O, N, S, etc.). Interestingly, some clusters contain also reduced Pd^I as revealed by the significant signals assigned to $[Pd_mCl_{2m}]^-$ anions. The amount of partial reduction neither depends on the ionization conditions nor the concentration of the feed solution. However, notable differences for the various cluster sizes are apparent (Fig. 5) with the largest amount of reduction for the hexanuclear clusters [15].

The formation of the reduced clusters is elucidated by a collision-induced dissociation (CID) experiment with the mass-selected cluster ion $[Pd_4Cl_8]^-$ as an example. In the corresponding CID spectrum (Fig. 6), two kinds of processes are observed, (i) loss of atomic chlorine concomitant with further reduction of the formal oxidation state in the $[Pd_4Cl_7]^-$ fragment (formally, a $Pd^I{}_2Pd^{II}{}_2$ compound) or (ii) cluster degradation via loss of neutral palladium(I) chloride to yield $[Pd_3Cl_7]^-$ which only contains formal Pd^{II}.

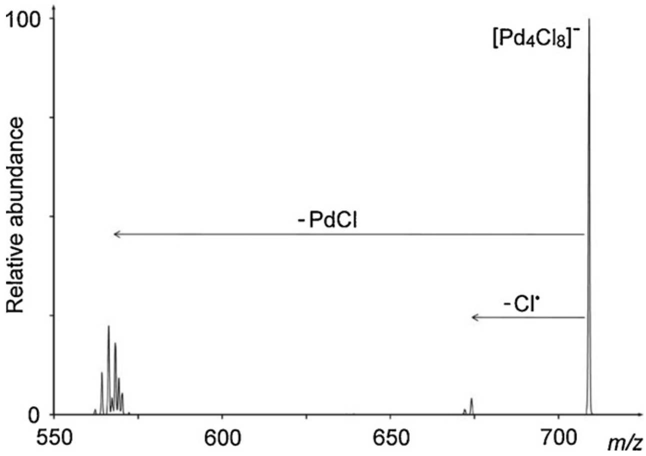

Fig. 6. Representative CID spectrum of mass-selected $[Pd_4Cl_8]^+$ with m/z 709 showing reduction associated with the loss of atomic chlorine as well as cluster cleavage via expulsion of neutral palladium(I) chloride. Due to the isotope patterns of Pd and Cl, the peak at m/z 709 is composed of several isotopomers and the fragment ion signals accordingly appear according to the corresponding isotope patterns of the elements involved.

Like for the cations, samples with analyte concentrations below 10^{-5} M give too weak signals for a quantitative evaluation in that only most abundant species are distinguishable from the noise. The measurements at higher concentrations confirm the results obtained in the positive ion mode in that the fractions of the various clusters sizes do not show a significant dependence from the concentration of the feed solution (Fig. 7).

3.3. Concentration dependences

The results obtained in this work for ESI of palladium(II) chloride solutions in acetonitrile reveal two surprises. At first, the absence of a concentration dependence of the distributions of the mono- and oligonuclear species is quite unexpected and demands for a rationale. Secondly, the partial reduction of the anionic clusters is of interest, because the reduction of Pd^{II} to lower valences is assumed as an important first step in palladium catalysis. Despite several quantitative differences in the cluster-ion distributions, Figs. 3 and 7 clearly demonstrate that the general phenomenon of clustering does not depend on the actual charge state, in that the monomeric species are comparably weak in both ionization modes.

With regard to the first observation, there exist at least two conceivable rationales. The large amount of clustering in both positive and negative ion mode together with the low total ion currents compared to other metal(II) salts [20,23,25,26,28,31,32,36] or palladium complexes with larger ligands [27,44,45] suggests a significant amount of aggregation of $PdCl_2$ in acetonitrile solution. Provided these aggregates were comprising larger numbers of palladium atoms, the ESI mass spectra would always sample only the fractional amount of smaller clusters, either present in solution or formed in the ESI process itself, despite the fact that we applied relatively soft ionization conditions. The second, related rationale evolves from the consideration that the low total ion currents may be regarded as an indication that the amount of heterolysis of $PdCl_2$ is small in acetonitrile. If this were true, most of the ions would be formed only in the ESI process itself at a critical droplet size and concentration with the consequence that the total concentration of the feed solution has a minor influence on the observed cluster ion distribution. Irrespective, which of these explanations holds true, it is obvious that the correlations between the ESI mass spectra and

Table 1
Concentrations (c), specific conductivities (k), molar conductivities (Λ), mean ion activity coefficients ($f_{\pm}$), degrees of association (y) and thermodynamic ion association constants (K_A) for $PdCl_2$ in acetonitrile at 21 °C.

$10^4\,c$ (M)	$10^6\,k$ (S cm^{-1})	Λ (S cm^2 mol^{-1})	$f_{\pm}$	y	K_A [a] (mol^{-1} l)
0.143	3.0	210.1	0.9994	0.0024	170
0.201	4.2	208.9	0.9992	0.0080	404
0.255	5.3	207.8	0.9992	0.0135	543
0.307	6.4	206.4	0.9991	0.0199	676
0.357	7.4	205.9	0.9990	0.0225	661
0.381	7.8	205.1	0.9990	0.0260	720
0.426	8.7	204.7	0.9989	0.0278	692
0.491	10.0	203.6	0.9988	0.0332	726
0.571	11.5	202.2	0.9987	0.0400	763
0.580	11.7	202.2	0.9987	0.0399	748
0.650	13.1	201.1	0.9987	0.0450	762
0.750	15.0	199.7	0.9986	0.0519	772
0.900	17.8	197.7	0.9984	0.0613	775
1.200	23.3	194.5	0.9982	0.0763	748
2.000	37.8	189.0	0.9976	0.1023	638
2.277	42.8	187.8	0.9975	0.1078	598

[a] K_A values determined for the association process $PdCl^+ + Cl^- \rightarrow PdCl_2$ by means of the Lee–Wheaton [46–48] model in the form suggested by Pethybridge and Taba [49] assuming that the center-to-center distance of the formed ion pairs is equal to Bjerrum's critical distance (0.78 nm) as suggested in the literature [50,51].

solution concentrations well-established for other systems do not apply for $PdCl_2/CH_3CN$.

To further elucidate this aspect, the conductivities of solutions of $PdCl_2$ in acetonitrile in the concentration range from 0.02 to 0.20 mM were measured at 21 °C (Table 1). The dependence of the molar conductivity from the square root of the electrolyte concentration was not linear even at relatively low concentrations, demonstrating a deviation from Kohlrausch's limiting law, which can be attributed to ionic atmosphere effects, the so-called relaxation or asymmetry and electrophoretic effects, as well as to ion association [52]. In essence, the increase of concentration results in a greater tendency for inter-ionic attractions (formation of either ion-pairs or aggregates), leading to decrease of the number of carriers of electric charge (free or "unassociated" ions) and retardation of their motion, causing a decrease in total molar conductivity. According to literature reports, symmetrical non-associated 1:1 electrolytes, such as the tetraalkylammonium salts, exhibit molar conductance values in the range of 120–160 S cm^2 mol^{-1} in acetonitrile (for $c \approx 1.0$ mM) [53,54]. For unsymmetrical electrolytes even larger conductivity values were measured, namely molar conductivities in the range of 200–300 S cm^2 mol^{-1} were reported for 2:1 salts in acetonitrile in the same concentration regime [40,55]. The somewhat smaller molar conductivities obtained for $PdCl_2$ (188–210 S cm^2 mol^{-1}, Table 1) indicate a larger tendency for aggregation in acetonitrile in comparison with other common 2:1 type electrolytes.

The conductivity data were analyzed by means of the Lee–Wheaton conductivity model [46–48] in the form suggested by Pethybridge–Taba [49] in order to determine the molar conductivity at infinite dilution Λ_o, where the ions are far apart and there are no inter-ionic attractions; for the approximations in this analysis, also see the comments in the experimental details. Using the same procedure, the thermodynamic ion association constant K_A for the process: $PdCl^+ + Cl^- \rightarrow PdCl_2$ was derived. Likewise, a limiting molar conductivity of $\Lambda_o = 210.6$ S cm^2 mol^{-1} was obtained for $PdCl_2$ in acetonitrile. As expected, a comparably large association constant was determined for $PdCl_2$ ($K_A = 664 \pm 40\,M^{-1}$), indicating significant aggregation already in solutions of low concentrations. The degree of association, namely the fraction of the ions existing as ion-pairs increases with the increase of the salt concentration, which is accordingly accompanied by a decrease of the molar conductance (Fig. 8). In comparison to other salts, it is interesting to note that even at low concentrations of about 0.2 mM, about 10% of the total palladium appears to be bound in ion-pairs.

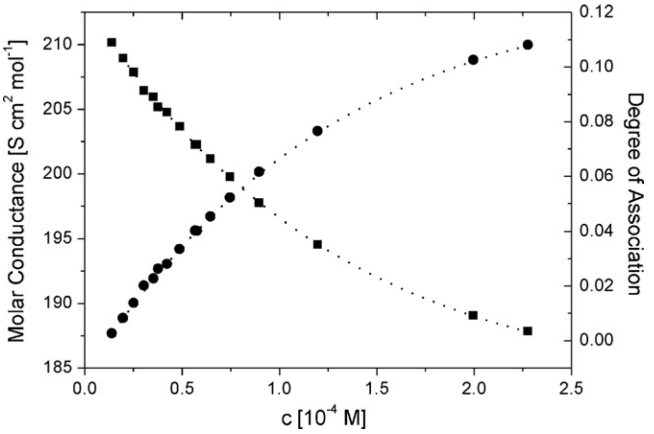

Fig. 8. Variation of the molar conductance (■) and the degree of association (●) of $PdCl_2$ with concentration in acetonitrile solution at 21 °C.

Given the significant amount of aggregation of $PdCl_2$ already in dilute acetonitrile solutions, we can in fact provide a tentative rationale for the results of the ESI experiments. In the electrospray process, the droplets of the solution are transferred to the mass spectrometer in the presence of nitrogen as a bath gas while passing a heated zone. As the solvent evaporates from the droplets, the concentration of the analyte increases. For systems with large association constants, this effect is relatively small, because the evaporation of the solvent is faster than the readjustment of the equilibrium [56]. For kinetically more labile ions the concentration increase can be more significant [57]. It is to be pointed out explicitly, however, that the details of the electrospray process for simple salt solutions are far from being really understood. For example, for the formation of cluster ions of the type $[Na_mCl_{m-1}(H_2O)_n]^+$ upon ESI of sodium chloride dissolved in water, which were first disputed [58], but then unambiguously detected [59–62], various suggestions involving different mechanisms for ion formation have been put forward [63,64], but none of the explanations really is comprehensive [65] and only recently the obvious lack of a clear rationale lead to the suggestion that the monomeric $Na(H_2O)_n{}^+$ cations and the $[Na_mCl_{m-1}(H_2O)_n]^+$ clusters originate from completely independent processes [66]. Recently has even been argued that ESI not at all samples the bulk solution, but only the droplet surfaces instead [67]. While this situation certainly demands for additional investigations on the electrospray process itself, several obvious correlations between ESI data and solution properties being observed in recent years [17,27–29,68–72] request for an intermediate, deliberately more pragmatic approach. To this end, we have recently proposed a merely phenomenological method via modeling of the concentration dependences according to which it is suggested that for the aggregation of simple metal salts in aqueous solution, the effective concentration in the spray process (c_{spray}) can exceed the concentration of the feed solutions (c_{feed}) by several orders of magnitude [29] and the correlation appears to hold true also for solutions in acetonitrile [27]. Moreover, the correlation factor f_{spray} in the empirical correlation $c_{spray} = f_{spray} \times c_{feed}$ rises for lower concentrations with the consequence that the differences in c_{feed} level out to a significant extent in c_{spray}. In the case of $UO_2(NO_3)_2$/water, for example, a range from 10^{-8} to 10^{-2} M in c_{feed} converted into a variation of only about 10^{-2}–10^{-1} M in c_{spray} [29]. Given the significant association of $PdCl_2$ as deduced from the conductivity studies, we accordingly conclude that the effective concentrations upon ESI of $PdCl_2$/acetonitrile reach a regime in which most of the palladium species are aggregated.

The concentration-independences in Figs. 3 and 7 are hence be attributed to a relatively narrow variation of c_{spray} in that it stays in a range in which large aggregates prevail. In parallel, despite the adjustment of soft ionization conditions, a significant degree of cluster degradation is assumed to occur in the ESI process itself, which affords the smaller clusters irrespective of the actual concentration. The latter conclusion indicates that in the case of $PdCl_2/CH_3CN$, the sampling of the solution via ESI is not "innocent" in that the clusters undergo fragmentation either in the spray itself or during the transport to the ion trap mass spectrometer.

4. Conclusions

The system palladium(II) chloride/acetonitrile is examined by means of ESI-MS. For cationic as well as anionic species, a pronounced tendency for the formation of oligonuclear clusters is deduced from the experiments. The cationic clusters are solvated with acetonitrile and have the general formula $[Pd_nCl_{2n-1}(CH_3CN)_m]^+$ in which the valence state of palladium is maintained. In contrast, binary palladium chlorides without any attached solvent molecules, i.e., $[Pd_nCl_{2n+1}]^-$, are observed in negative ion mode along with a significant amount of reduced species which have lost one of more chlorine atoms. By means of complementary conductivity measurements in solution, the interesting observation that the size distribution of cluster ions sampled with ESI does not significantly depend on the concentration of the feed solutions is attributed to a pronounced aggregation in the concentration range studied in conjunction with some cluster degradation in the spray process. In a more general perspective, the present results indicate that solutions of $PdCl_2$ in organic solvents such as acetonitrile cannot be treated as simple mononuclear solvates, because already at relatively low concentrations pronounced aggregation to oligonuclear clusters is observed. With regard to the widespread synthetic use of $PdCl_2$ in homogeneous catalysis, consideration of clusters rather than monodisperse species therefore is worth further attention.

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