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Substitution reactions of some novel sterically hindered monofunctional Pd(II) complexes

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ABSTRACT

Substitution reactions of the monofunctional complexes $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$, where TL^{tBu} = 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine and tpdm = terpyridinedimethane, with nucleophiles such as: thiourea, I^-, Br^-, NO_2^-, pyridine and dimethyl-sulfoxide (DMSO) were studied in 0.1 M $NaClO_4$ aqueous solution in the presence of 10 mM NaCl. The reactions were carried out at three different temperatures (288, 298 and 308 K) using a variable-temperature stopped-flow technique. The substitutions were followed under the *pseudo*-first-order conditions with a large excess of nucleophiles. Obtained results show that the complex with tpdm ligand reacts faster than the complexes with TL^{tBu} ligand due to the bulkiness of the inert tridentate ligands. Also, the presence of *t*-Bu groups on the terminal imadazole rings of TL^{tBu} ligand significantly slow down the rate of the substitution. The order of reactivity of used ligands is: thiourea > I^- > Br^- > NO_2^- > pyridine > DMSO. This order is in agreement with their electronic and structural characteristics. The negative values reported for the entropy of activation confirmed the associative substitution mode. These results are discussed in order to find the connection between the structure and reactivity of the complexes with tridentate sterically hindered ligands.

1. Introduction

Coordination compounds of palladium(II) with tridentate ligands such as diethylentriamine (dien), bis(2-pyridylmethyl)amine (bpma) or 2,2′:6′,2-terpyridine (terpy) provide very useful substrates for studies on ligand substitution reactions of square-planar complexes [1–6,21,22]. It is well known that relatively small structural modifications in a multidentate ligand can produce significant changes in the reactivity of the complexes [7–9].

There is a high interest among scientists nowadays in the field of the steric and electronic tuning of the lability of square-planar Pd(II) complexes as well as their influence on the interaction between such complexes and bio-relevant nucleophiles and DNA fragments [10]. Furthermore, some mixed ligand palladium(II) complexes have shown to act as potential anticancer agents [11–16].

Recently Zhang et al. synthesized a number of Pd(II) complexes with unusual ligand 4-toluenesulphonyl L-amino acid and bipy or phen which show antitumor activity in cancer cell lines [17]. In addition Pd(II) complex with *N*-(chlorophenyl)-3-pyridinecarboxamide ligand has a *trans* geometry and could be coordinated to DNA [18]. Furthermore, Pd(II) complexes generally formulated as *trans*-$[PdX_2(isn)_2]$, where X = Cl^-, N_3^-, SCN^- or NCO^- and isn = isonicotinamide have very small anticancer but significant antituberculous activity [19] while complexes with amino alcohols, such as L-prolinol, L-valinol, L-isoleucinol show certain antitumor activity [20].

As a part of our interest in the synthesis, structure and reactivity of coordination complexes of Pd(II) with chelating ligands [1–6,21,22] and with the aim to contribute towards our previously published work, we synthesized novel tridentate nitrogen-donor ligands TL^{tBu} = 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl] pyridine and tpdm = terpyridinedimethane and the corresponding Pd(II) complexes, $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ [23,24]. We studied and report here complex formation of $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ with different nucleophiles (Fig. 1) in 0.1 M $NaClO_4$ aqueous solution and in the presence of 10 mM NaCl to prevent spontaneously hydrolysis.

2. Experimental

2.1. Materials and methods

The ligands thiourea (Kemika, Zagreb), NaI, KBr, $NaNO_2$, pyridine (Zorka, Šabac) dimethylsulfoxide (DMSO) (Fluka) were used without further purification. The complexes $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ were prepared according to published procedures [23,24]. Prepara-

Abbreviations: TL^{tBu}, 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine; tpdm, terpyridinedimethane.

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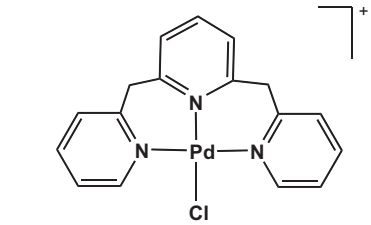
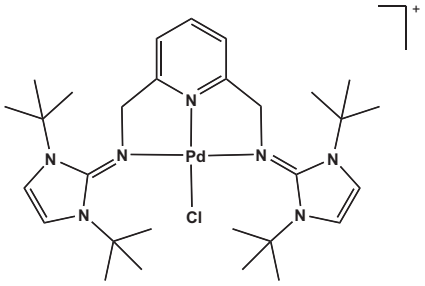


[Pd(tpdm)Cl]$^+$



[TL$^{t\mathrm{Bu}}$PdCl]$^+$

Fig. 1. The structures of investigated complexes.

tion of the ligands TL$^{t\mathrm{Bu}}$ and tpdm has been also previously published [25,26]. All the other chemicals were of the highest purity commercially available.

2.2. Instrumentation

UV–Vis spectra were recorded on Perkin Elmer Lambda 25 spectrophotometers with thermostated 1.00 cm quartz Suprasil cells. Kinetic measurements were performed on an Applied Photophysics SX.18 stopped-flow instrument coupled to an online data acquisition system. The temperature was controlled throughout all kinetic experiments to ±0.1 K.

2.3. Kinetic measurements

The substitution reactions of the [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ and [Pd(tpdm)Cl]$^+$ complexes with the nucleophiles: thiourea, I^-, Br^-, NO_2^-, pyridine and DMSO were studied spectrophotometrically by following the change in absorbance at suitable wavelengths as a function of time. Spectral changes were recorded over the range from 200 to 400 nm to establish a suitable wavelength at which kinetic measurements could be performed. Substitution reactions of [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ and [Pd(tpdm)Cl]$^+$ complexes were initiated by mixing equal volumes of complex and ligand solutions directly in the stopped-flow instrument and the reaction was followed for at least eight half-lives. The substitution process was monitored as change in absorbance with time under *pseudo*-first-order conditions.

All substitution reactions were studied in 0.1 M $NaClO_4$ aqueous solution. The $NaClO_4$ was taken because it is well known that perchlorate ions do not coordinate to Pt(II) or Pd(II) in aqueous solution [27]. To the solution was added 10 mM NaCl to prevent the spontaneous hydrolysis of the complexes.

The temperature dependence of the second-order rate constants was studied for the reactions of [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ complex with I^- and pyridine and for the [Pd(tpdm)Cl]$^+$ complex with I^-, Br^-, pyridine and DMSO.

The observed *pseudo*-first-order rate constants, k_{obs}, were calculated as the average value from four to eight independent kinetic runs using the program ORIGINPRO 8. Experimental data are reported in Tables S1–S11 (Supplementary material).

3. Results and discussion

Substitution reactions of the [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ and [Pd(tpdm)Cl]$^+$ complexes proceeds according to Scheme 1.

Substitution reactions of square-planar metal complexes proceed according to two parallel pathways [28]. One involves the formation of a solvent-coordinated complex, followed by rapid substitution of the coordinated solvent molecule by the entering nucleophile (solvolytic pathway), and the other involves direct nucleophilic attack by the entering nucleophile. In the present study direct nucleophilic attack proceeds in a reversible manner as suggested in Scheme 1. Under *pseudo*-first-order conditions, these rate constants can be determined from the plot of the linear dependence of k_{obs} versus total nucleophile concentration, according to the Eq. (1). The slope of the line represents k_2, whereas the intercept represents $k_1[Cl^-]$. All kinetic data are summarized in Tables S1–S11 (Supporting information, ESI).

The observed pseudo-first order rate constant, k_{obs}, as a function of total ligand concentration is given by Eq. (1).

$$k_{obs} = k_2[L] + k_1[Cl^-] \quad (1)$$

Direct nucleophilic attack is characterized by the rate constants k_2, and the reverse reactions are presented by the rate constants k_1. The second-order rate constant k_2, characterizing the formation of the product, can be evaluated from the slope of a plot k_{obs} versus ligand concentration. The experimental results for the displacement of chloride ion from [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ and [Pd(tpdm)Cl]$^+$ complexes are summarized in Table 1. Representative plots are shown in Figs. 2–5 (others are given in Supplementary material, Figs. 1S–7S). As can be seen in all cases $k_{obs,}$ depends linearly of the entering ligand concentration.

According on the values of k_2, from the Table 1, the used nucleophiles are good entering ligands for the substitution reactions of the Pd(II) complexes. Comparing the reactivity of the nucleophiles we observed that the reactivity decreases in the following order: thiourea > I^- > Br^- > NO_2^- > pyridine > DMSO.

It is generally known that the Pt(II) and Pd(II) complexes have a very high affinity towards nucleophiles containing S-donor atoms. Recently published rate constants for the substitution reactions of some Pd(II) complexes with sulfur-donor nucleophiles are very high [29,30] whereas the highest reactivity shows thiourea compared to the other used ligands. Thiourea is a very useful nucleophile since it combines the ligand properties of thiolates (σ-donor) and thioethers (σ-donor, π-acceptor) [22,24] so it shows the strongest nucleophilicity. Our results confirm this explanation. Better reactivity of I^- ion compared to that of Br^- and NO_2^- ions can be explained by different polarizability of these nucleophiles. Namely, iodide ion is the most polarized halide ion (4.7×10^{-24} cm^3) [31], so it can be classified as "the softest" halide ion. "Soft" (polarizable) nucleophile favors "soft" substrate. Since Pd(II) is a "soft" acid its high reactivity with iodide is not surprising [32]. The polarizability of the Br^- is 3.05×10^{-24} cm^3 [31], so this ion is also "soft" base, but less "soft" than iodide. This is the main reason for the lower reactivity of bromide. Since NO_2^- ion is a "transition hard-soft" base, we expected and observed lower reactivity compared to that of halide

$$[(X)PdCl]^+ + L \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [(X)PdL]^{z+} + Cl^-$$

X = TL ^{Bu}, tpdm

L= thiourea, I$^-$, Br$^-$, DMSO, pyridine, NO_2^-

Scheme 1. Schematic presentation of the substitution reactions of the [(TL$^{t\mathrm{Bu}}$)PdCl]$^+$ and [Pd(tpdm)Cl]$^+$ complexes with nucleophiles: thiourea, I^-, Br^-, NO_2^-, pyridine and DMSO.

Table 1
Rate constants and activation parameters for the substitution reactions of $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ complexes with different nucleophiles in 0.1 M $NaClO_4$ and 10 mM NaCl.

$[Pd(tpdm)Cl]^+$		k_2 (M^{-1} s^{-1})	$k_1[Cl^-]$ (M^{-1} s^{-1})	$\Delta H_2^{\neq}$ (kJ mol^{-1})	$\Delta S_2^{\neq}$ (J K^{-1} mol^{-1})
Thiourea[a]	**298**	(**5.8** ± **0.2**) × 10^3	0.37 ± 0.08	29 ± 3	−75 ± 8
I^-	288	526 ± 3	12 ± 1		
	298	**646** ± **5**	47 ± 2	8 ± 3	−180 ± 9
	308	693 ± 6	230 ± 5		
Br^-	288	43 ± 1	3.2 ± 0.1	/	/
	298	**90** ± **2**	26 ± 1		
NO_2^-	**298**	**63.5** ± **0.5**	30 ± 1	/	/
Pyridine	288	25.1 ± 0.1	(3.6 ± 0.1) × 10^{-1}	31 ± 7	−120 ± 20
	298	**47.5** ± **0.2**	5.0 ± 0.1)		
	308	61.9 ± 0.2	39 ± 2		
DMSO	288	40.4 ± 0.5	7.0 ± 0.1		
	298	**47** ± **1**	16 ± 1	10 ± 1	−195 ± 3
	308	56 ± 2	30 ± 2		
$[Pd(TL^{tBu})Cl]^+$					
Thiourea	**298**	(**1.3** ± **0.3**) × 10^3	39 ± 2	/	/
I^-	288	49 ± 1	1.3 ± 0.1		
	298	**79** ± **1**	13.8 ± 0.1	22 ± 6	−150 ± 20
	308	95 ± 2	20.2 ± 0.2		
Br^-	**298**	**22.1** ± **0.4**	21 ± 1	/	/
NO_2^-	**298**	**14** ± **2**	23 ± 1	/	/
Pyridine	288	12.8 ± 0.5	1.4 ± 0.1		
	298	**13.6** ± **0.5**	2.8 ± 0.1	10 ± 5	−205 ± 15
	308	17.8 ± 0.8	4.0 ± 0.2		
DMSO	**298**	**10.9** ± **0.5**	24 ± 2	/	/

[a] Ref. [24].

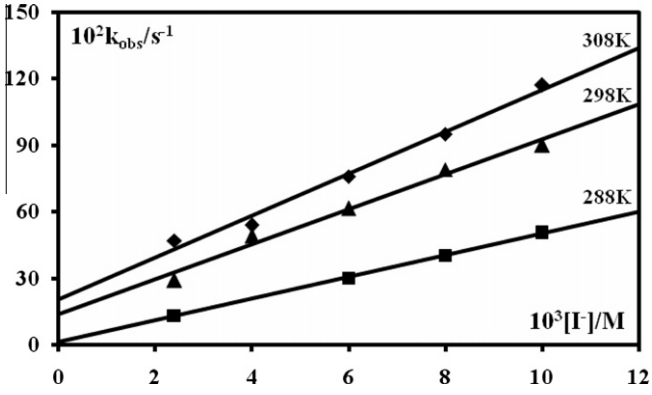


Fig. 2. *Pseudo*-first order rate constants, k_{obs}, as a function of ligand concentration and temperature for the substitution reactions of $[(TL^{tBu})PdCl]^+$ complex with I^- in 0.1 M $NaClO_4$ and 10 mM NaCl.

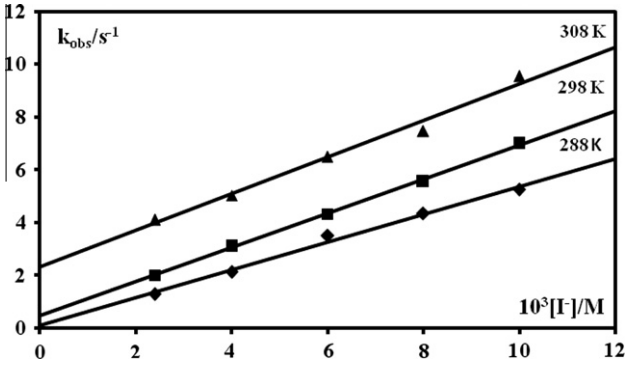


Fig. 4. *Pseudo*-first order rate constants, k_{obs}, as a function of ligand concentration and temperature for the substitution reactions of $[Pd(tpdm)Cl]^+$ complex with I^- in 0.1 M $NaClO_4$ and 10 mM NaCl.

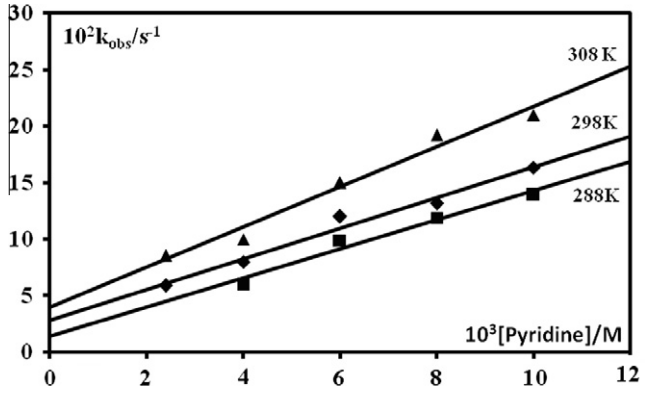


Fig. 3. *Pseudo*-first order rate constants, k_{obs}, as a function of ligand concentration and temperature for the substitution reactions of $[(TL^{tBu})PdCl]^+$ complex with pyridine in 0.1 M $NaClO_4$ and 10 mM NaCl.

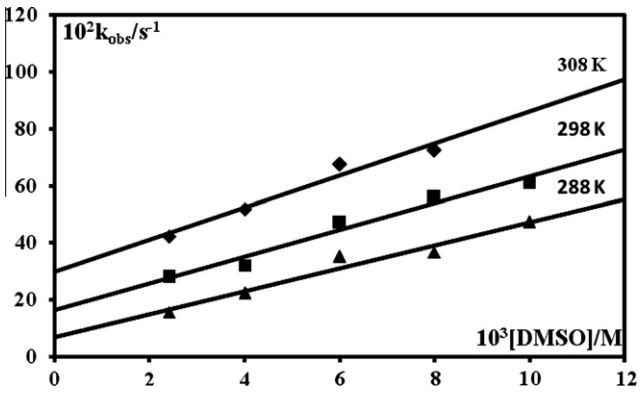


Fig. 5. *Pseudo*-first order rate constants, k_{obs}, as a function of ligand concentration and temperature for the substitution reactions of $[Pd(tpdm)Cl]^+$ complex with DMSO in 0.1 M $NaClO_4$ and 10 mM NaCl.

ions. Small reactivity of DMSO was also expected since DMSO has a specific feature. It has two donor atoms. In studied reactions DMSO is first coordinated through the oxygen atom, where the negative partial charge is localizes. Than, the Pd(II)–O bond breaks forming the thermodynamically more stable sulfur-coordinated product. On the other side, the bulkiness of two methyl groups in the molecule of DMSO as well as the bulkiness of the inert tridentate ligands in the structure of the studied complexes could prevent the formation of the metal–ligand bond and slow down the rate of the substitution. The reactivity of pyridine is almost the same as that for DMSO. Here we have a competition between the type of donor atom and size of the entering ligand.

The reactivity of the studied complexes toward selected nucleophiles is determined from the data of the rate constants (Table 1). The $[Pd(tpdm)Cl]^+$ complex reacts faster than $[(TL^{tBu})PdCl]^+$ complex (approximately three times). Both complexes have a sterically hindered inert tridentate ligand. But, the presence of *tert*-butyl groups in the structure of $[(TL^{tBu})PdCl]^+$ complex has a significant influence on the decreasing of the substitution rate.

Having in mind that these complexes are novel, for better understanding of their characteristics we compared the rate constants for the substitution reactions with I^- with earlier published values for some other sterically crowded monofunctional Pd(II) complexes, Table 2. According to the values for the *second*-order rate constant can be concluded that both complexes $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ have the reactivity between those of $[Pd(1,4,7\text{-}Et_3dien)Cl]^+$ and $[Pd(1,1,4\text{-}Et_3dien)Cl]^+$ complexes [22].

The reactivity of the complexes that contain inert tridentate NNN-donor ligands with pyridine rings largely depends on the number and arrangement of the pyridine rings [33]. For example, in the case of the terpy chelate, there is strong interaction between the metal ion and the pyridine rings, especially with the central pyridine ring in the terpy chelate, resulting in a strong *trans*-effect and very fast substitution reactions. In contrast, $[PdCl(dien)]^+$ does not contain pyridine rings and react much more slowly. The studied $[Pd(tpdm)Cl]^+$ complex also includes pyridine rings, but in the tridentate tpdm ligand they are separated by methylene groups, so the system is more flexible in comparison with terpyridine. This is confirmed by the crystal structure of the $[Pd(tpdm)Cl]^+$ complex [24]. Observed results clearly illustrate that a relatively small structural modification of the tridentate ligand has a strong influence on the reactivity of the complex.

In order to determinate the affinity of $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ complexes towards studied nucleophiles, a Linear Free Energy Relationship (LFER) was used. The relationship between second-order rate constant, k_2, and nucleophilicity constants of the nucleophiles (n^0_{Pt}) is given by Eq. (2) while the values of $\log k_2$ and n^0_{Pt} are given in Table 12S.

$$\log k_2 = sn^0_{Pt} + \log k_s \quad (2)$$

A plot of $\log k_2$ against the nucleophiles nucleophilicity constants (n^0_{Pt}) is shown in Fig. 6.

Since the points appear approximately on a straight line, it is an indication that the substitution of a chloride ion from studied complexes by selected nucleophiles occurs *via* the same mechanism (Fig. 6.). The slop of the line presents the *s* value, which represents degree of affinity of the complex towards the nucleophiles. The *s* values for $[(TL^{tBu})PdCl]^+$ complex is 0.47 and for $[Pd(tpdm)Cl]^+$ complex is 0.51. These values are lower than the value of the standard substrate *trans*-$[Pt(py)_2Cl_2]$ ($s = 1.00$) [34]. This means that studied $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ complexes are less discriminated in comparison with *trans*-$[Pt(py)_2Cl_2]$ complex for the substitution reactions with different nucleophiles. The $[(TL^{tBu})PdCl]^+$ has a slightly lower discriminating factor, so it reacts slower than $[Pd(tpdm)Cl]^+$, what is in agreement with experimentally observed results.

The sensitivity of the rate constants on the nature of the entering ligands and the negative entropies of activation given in Table 1 indicates that the substitution reactions proceed *via* an associative mode of activation.

Table 2
Second order rate constants, k_2, for the substitution reactions of series of different $[Pd(L)Cl]^+$ complexes with I^- at 298 K.

L	k_2 (M^{-1} s^{-1})	Ref.
tpdm	646 ± 5	This work
TL^{tBu}	79 ± 1	This work
Dien	4446 ± 41	[22]
1,4,7-Me_3dien	3542 ± 319	[22]
1,4,7-Et_3dien	932 ± 4	[22]
1,1,4-Et_3dien	21.2 ± 0.3	[22]
1,1,7,7-Me_4dien	0.28 ± 0.53	[22]
1,1,7,7-Et_4dien	8.0×10^{-4}	[22]

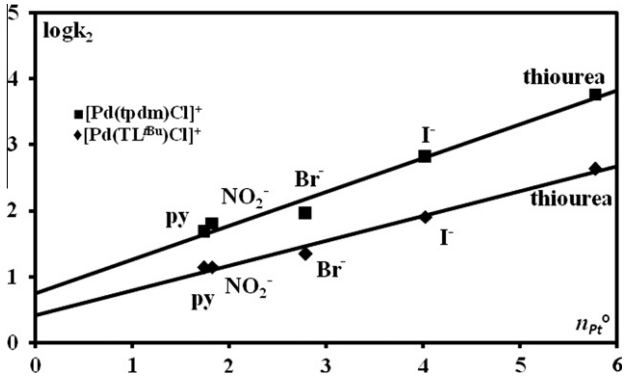


Fig. 6. Linear Free Energy Relationship of $[(TL^{tBu})PdCl]^+$ and $[Pd(tpdm)Cl]^+$ complexes with different nucleophiles.

4. Conclusion

The substitution reactions of two novel Pd(II) complexes containing different chelating inert ligands with selected nucleophiles were investigated. The obtained results show that the nature of entering ligand as well as the nature of the inert tridentate ligand play an important role in the kinetic behavior of the Pd(II) complexes. These results also show that the complex with tpdm ligand reacts faster than the complex with TL^{tBu} ligand, which could be explained by the bulkiness of the inert tridentate ligands. Namely, the presence of *t*-Bu groups on the terminal imadazole rings of TL^{tBu} ligand significantly prevent the substitution. The order of reactivity of entering ligands is: thiourea > I^- > Br^- > NO_2^- > pyridine > DMSO. The mechanism of the substitution reactions is associative supported by the negative values of $\Delta S^{\neq}$.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.031.

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