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Comparison of MALDI-TOF mass spectra of [PdCl(dien)]Cl and $[Ru(en)_2Cl_2]Cl$ acquired with different matrices

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Abstract: In this work, the matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectra of two cationic complexes, *i.e.*, [PdCl(dien)]Cl and $[Ru(en)_2Cl_2]Cl$, acquired under different conditions were analyzed. The spectra were recorded with three matrices with or without trifluoroacetic acid (TFA), *i.e.*, two traditional matrices, *i.e.*, 2,5-dihydroxybenzoic acid and α-cyano-hydroxycinnamic acid, and one flavonoid, quercetin. The spectra acquired with quercetin appeared to be the simplest, whereas in the spectra obtained with other matrices, peaks arising either from the addition of matrix molecules or from the fragmentation products were detectable. Addition of TFA did not complicate the spectra of the Pd(II) and Ru(III) complexes when the traditional matrices were used. On the other hand, the spectra of Pd complex were simpler, whereas the addition of TFA in the case of the Ru complex resulted in a higher number of peaks, some of which could not be identified. Taken together, the results of this study once more emphasize the differences arising in the MALDI-TOF mass spectra of transition metal complexes in dependence on the applied matrix.

Keywords: MALDI-TOF MS; metallo-drugs; matrix; peak assignment.

INTRODUCTION

There are serious scientific efforts aimed at synthesizing new transition metal complexes as potential candidates for antitumor therapeutics but which exhibit fewer toxic effects than the well-established platinum complexes.[1–4] Pd(II) complexes are usually very good model compounds for mechanistic investigations since they exhibit a 10^4 to 10^5 fold higher reactivity than the well-known Pt(II) antitumor complexes, whereby their structural and equilibrium behavior are

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rather similar.[5] In addition, a number of Ru(III) complexes showed promising antitumor and antimetastatic activity.[6,7]

Several methods can be used for the analysis and characterization of transition metal complexes, as well as for monitoring their possible interaction with biomolecules; among them, matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS) seems to be a promising tool, due to its capability of analyzing both transition metal complexes and biomolecules.

Generally, mass spectrometry has been routinely applied for the analysis of metal complexes. For instance, fast atom bombardment (FAB) MS has been applied for the analysis of platinum(II) and platinum(I) dinuclear hybrids.[8] In addition, a combination of various MS ionization methods, such as electron ionization (EI), FAB and MALDI, provides important structural information.[9]

Mild ionization techniques, *i.e.*, those which yield fewer fragmentation products, such as electrospray ionization (ESI) and MALDI,[10] are not only suitable for the analysis of high mass molecules, but have also found their application in the analysis of inorganic compounds. MALDI was used for the characterization of transition metal complexes,[11,12] and for monitoring the interaction of platinum drugs with different molecules, such as poly(ethylene glycol)[13] and polystyrene,[14] as well as with biological systems.[15–17]

Choice of the matrix for the MALDI-TOF MS analysis is an important issue since the matrices used for MALDI-TOF mass spectrometric analysis of transition metals complexes exhibit certain drawbacks, as was recently described.[18–20] On the other hand, flavonoids, when used as matrices for MALDI-TOF MS seem to stabilize Pt, Pd and Ru complexes and enable reproducible and reliable analysis of these compounds.[18,20] This is an advantage over the other more commonly used methods, since in most cases the ligand–metal bond is preserved when flavonoids were used as matrices and little or no fragmentation could be detected. Although being good matrices for transitional metal complexes, flavonoids cannot be used as matrices for MALDI-TOF MS analysis of biomolecules; the application of more "traditional" matrices for this purpose is still required.

The main aim of this work was to analyze the spectra of two cationic complexes ([PdCl(*dien*)]Cl and [Ru(*en*)$_2$Cl$_2$]Cl) obtained with the assistance of traditional matrices (DHB and CHCA) and one selected flavonoid, *i.e.*, quercetin. Moreover, the positive ion MALDI-TOF mass spectra in more acidic environments, *i.e.*, addition of trifluoroacetic acid (TFA) to the matrix solution, which was shown to result in better signals for biomolecules, were also analyzed.[21]

EXPERIMENTAL

Chemicals

Paladium(II) and ruthenium(III) complexes: [Pd(dien)Cl]Cl (diethylenetriamine paladium(II) chloride) (*Mr* = 280.5) and [Ru(en)$_2$Cl$_2$]Cl (dichlorido (ethylenediemine)ru-

thenium(III) chloride) (*Mr* = 327.6) were synthesized as described in the literature.[23,24] Chemical analysis, UV–Vis and ^{1}H-NMR spectral data of these complexes were in good agreement with those obtained in previous preparations. TFA, matrices for MALDI-TOF MS, *i.e.*, 2,5-DHB and α-CHCA, were purchased from Sigma-Aldrich (München, Germany) and were applied without further purification. Quercetin dihydrate (≥ 98 %) was also purchased from Sigma-Aldrich (Munich, Germany) and was used without further purification.

Methods

Preparation of the samples for MALDI-TOF MS. The metal complexes were dissolved in a combination of methanol/physiological solution (0.9 % NaCl) at the following concentrations: [Pd(dien)Cl]Cl, 8.62×10^{-3} M (50 % methanol/50 % physiological solution) and $[Ru(en)_2Cl_2]Cl$, 6.1×10^{-3} M (50 % methanol/50 % physiological solution). The matrices, 2,5-DHB and α-CHCA, were prepared prior to use. The following solutions of the matrices were used: 0.5 M 2,5-DHB in methanol and 5 mM α-CHCA in acetonitrile/water (1:1, v/v). For some experiments, a small amount of TFA (0.1 % final concentration) was added to the matrix solution.

The following approach was used for the application of the sample onto the MALDI target: a small volume (0.5 μL) of the solution of a metal complex was applied onto the sample plate, which was followed by immediate addition of the same volume of a matrix solution (DHB, CHCA or quercetin). The mixture was then left at room temperature to co-crystallize. This approach was shown to result in the best quality of MALDI-TOF mass spectra, as demonstrated in previous studies.[19,21]

MALDI-TOF MS. The MALDI-TOF mass spectra were acquired on a Voyager Biospectrometry DE Pro workstation (Perseptive Biosystems, Framingham, MA, USA). The system utilizes a 20 Hz pulsed nitrogen laser emitting at 337 nm. The spectra were acquired without a low mass gate and under delayed extraction conditions in the reflector mode. All spectra represent the average of 400 single laser shots. The laser intensity was kept sufficiently low to prevent degradation of the flavonoids and to obtain a good signal-to-noise ratio of the analyte.

Theoretical presentation of the mass spectra. Theoretical presentation of the spectra was realized with the assistance of the Selket program, version 1.4, available online.

RESULTS AND DISCUSSION

MALDI-TOF MS has been proven itself to be a useful method for the analysis of biomolecules. The most used matrices for the MALDI-TOF MS analysis of various classes of biomolecules are α-cyano-hydroxycinnamic (CHCA), synapinic acid (SA), and dihydroxybenzoic acid (DHB).[21] Although matrices usually serve as an assistance for the desorption/ionization process, they also yield signals in the mass spectra,[24] which, in certain cases, might overlap with peaks of interest.

Therefore, the first aim in the present study was to assign matrix peaks, in order to make the identification of peaks arising from an analyte more certain. This is particularly important when newly synthesized and not yet fully characterized transition metal complexes, as well as their interaction with various biomolecules, are to be studied by MALDI-TOF MS. In the second part of the work, the MALDI-TOF mass spectra of Pd(II) and Ru(III) complexes were analyzed and differences in the relation to the matrix used are discussed. Finally, the effect

of the laser intensity on the signal intensity of the positive ion mass spectra of the selected complexes in relationship with the chosen matrix is addressed.

LDI-TOF MS of DHB, CHCA and quercetin

Spectra of matrices used in this study are given in Fig. 1: in Figs. 1a and 1b the spectra of DHB are presented without and with TFA, respectively; Figs. 1c and 1d represent the positive ion mode LDI-TOF mass spectra of CHCA, also without and with TFA, respectively; the trace in Fig. 1e is the positive ion mode spectrum of quercetin and for the spectrum given in Fig. 1f, small amount of TFA was added. The identities of the peaks detected in the presented spectra are listed in Table I, and they will not be discussed here in more detail.

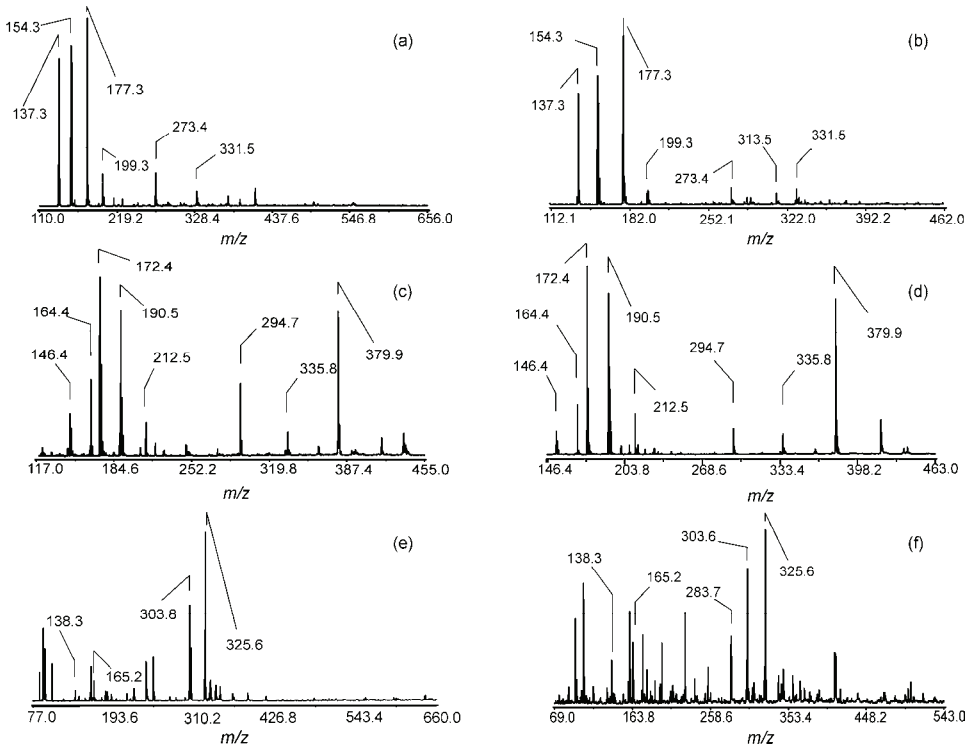

Fig. 1. Positive ion mode LDI-TOF mass spectra of DHB without and with TFA (a and b, respectively), CHCA without and with TFA (c and d, respectively) and quercetin, also recorded without and with TFA (e and f, respectively). Peaks are indicated according to their *m/z* position and their identities are given in Table I.

In agreement with previously published data,[24] the most intense peaks in the positive ion mode LDI-TOF mass spectra of DHB appeared at *m/z* = 137.3, 154.3 and 177.3. These peaks are generated either by the loss of a water molecule followed by addition of a proton, addition of a proton, or addition of a sodium ion

(Figs. 1a and 1b; *cf.* Table I), respectively. After the addition of TFA to the solution of DHB, neither significant differences in quality of mass spectra nor the number of peaks could be detected.

TABLE I. Peaks detected in the positive ion MALDI-TOF mass spectra of the used matrices. The corresponding spectra are given in Fig. 1; "M" corresponds to the molecule; the fragmentation pattern of quercetin is given in the literature[25]

Matrix	*m/z*	Peak assignment
2,5-DHB	137.3	$M - H_2O + H^+$
	154.3	M
	177.3	$M + Na^+$
	199.3	$M - H^+ + 2Na^+$
	273.4	$2M - 2H_2O + H^+$
	313.5	$2M - H_2O + Na^+$
	331.5	$2M + Na^+$
α-CHCA	146.4	$M - CO_2 + H^+$
	164.4	$M - CN + H^+$
	172.4	$M - H_2O + H^+$
	190.5	$M + H^+$
	212.5	$M - H^+ + Na^+$
	294.7	$2M + H^+ - CCNCOOH$
	335.8	Not assigned
	379.9	Not assigned
Q	138.3 and 165.2	$^{0,2}M^{+\#}$
	283.7	$M - H_2O + H^+$
	303.6	$M + H^+$
	325. 6	$M + Na^+$

The addition of TFA to the solution of CHCA did not significantly change the pattern of the LDI-TOF mass spectra of this matrix; neither did it result in an increase in the intensities of the peaks. The most expressed peaks in the spectra of CHCA were detectable at *m/z* = 172.4 ($M - H_2O + H^+$), *m/z* = 190.5 ($M + H^+$) and at *m/z* = 379.9, which has not been assigned so far (Figs. 1c and 1d; *cf.* Table I for peak assignment).

On the other hand, new peaks appeared in the spectra of quercetin after the addition of TFA (Fig. 1e without TFA, Fig. 1f with TFA). The most intense peaks in the spectra of quercetin correspond to the protonated and sodiated adducts of quercetin (peak at *m/z* = 303.8 and at *m/z* = 325.6, respectively). Certain high-intensity peaks could be assigned to possible degradation products of quercetin induced by the laser in the acidic solution, most probably according to pattern given in the footnote to Table I (*cf.* Table I). A number of undefined peaks were also detectable in the spectra of quercetin, irrespective of the presence of TFA, which leads to the assumption that quercetin combined with TFA might not be a good choice for MALDI-TOF MS analysis of transition metal complexes, at

least not under the conditions applied in this study. This finding might seem to be in contradiction to a previous work,[18] in which the addition of TFA did not lead to the fragmentation of quercetin. The possible reason for this might be the difference in the employed solvents: in the previous work, an aqueous suspension of quercetin was used as the matrix, whereas in this work, a methanolic solution of quercetin was preferred in an attempt to increase the miscibility with the methanolic solutions of the transition metal complexes. This difference in the solutions might result in the different behavior of this flavonoid under laser irradiation.

Theoretical presentation of the mass spectra of the Pd(II) and Ru(III) complexes

Each peak in the MALDI-TOF mass spectra actually represents a group of signals resulting from a number of combinations of naturally occurring isotopes. This is particularly expressed when the spectra are acquired in the reflector mode. Such a picture is in the case of transition metals and their complexes is even more complicated, since transition metals have a large number of natural isotopes. Therefore, before considering the experimental spectra, a theoretical presentation of the mass spectra of the used complexes will be briefly described.

Figure 2 represents theoretical presentations of the mass spectra of [Pd(en)Cl]Cl on the left and $[Ru(en)_2Cl_2]Cl$ on the right panel. These spectra are given for the purpose of reference and only a few signals are indicated. Figure 2 is accompanied by Table II, which contains a list of the isotopes of Pd and Ru, with their natural abundances.

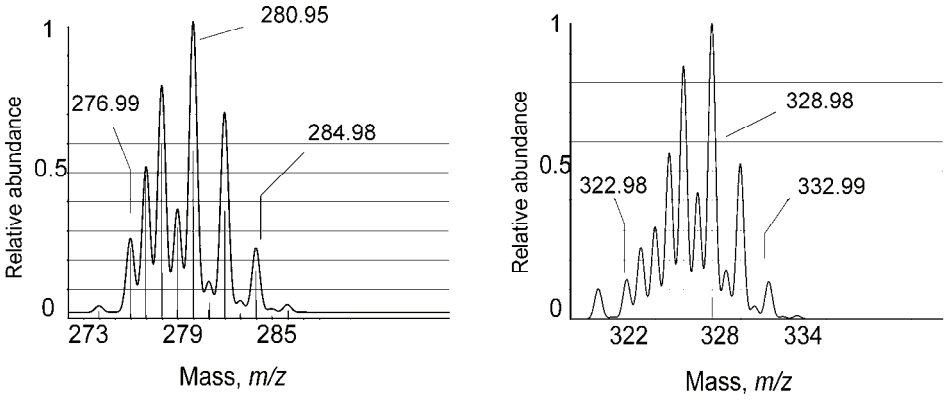

Fig. 2. Theoretical presentation of the mass spectra of Pd(II) (left panel) and Ru(III) complex (graph on the right). The spectra were created using the Selket program.

Pd has 6 naturally occurring isotopes with masses ranging from 101.91 to 109.91, whereas Ru has 7 (from 95.91 to 103.91). The most abundant isotope of Pd is the one with the mass 105.90 and that of Ru has the mass 101.90. It is easy to assume that the spectrum of both transition metal complexes will be even more

complex since a large number of isotope combinations (Pd, or Ru with C, N, H or Cl) are possible: the theoretical spectrum of the Pd complex contains 10 peaks, whereas that of Ru has 12 peaks.

TABLE II. List of isotopes of Pd and Ru and their natural abundance. The data were taken from the Selket program

Metal	Relative molar mass	Probability (abundance)
Pd	101.91	0.0373216245883644
	103.90	0.407610684229784
	104.91	0.817050859860959
	105.90	1
	107.90	0.968166849615807
	109.91	0.428832784485913
Ru	95.91	0.175
	97.91	0.0591772151898734
	98.91	0.401898734177215
	99.90	0.39873417721519
	100.91	0.541139240506329
	101.90	1
	103.91	0.588607594936709

In this study, it was decided to take the most intense peak in each peak group of the MALDI-TOF mass spectra of the Pd and Ru complexes for further discussion.

MALDI-TOF MS Analysis of the [Pd(dien)Cl]Cl complex

The positive ion MALDI-TOF mass spectra of [Pd(*dien*)Cl]Cl are given in Fig. 3: the spectra acquired with the assistance of DHB without and with TFA are given in Figs. 3a and 3b respectively; the spectrum of the same complex with CHCA without TFA is shown in Fig. 3c and in Fig. 3d spectrum acquired after the addition of TFA; the spectra in Figs. 3e and 3f represent the positive ion mode MALDI-TOF mass spectra of the same complex recorded with quercetin as the matrix without and with TFA, respectively. The identity of the peaks arising from the metal complexes analyzed in this study is overviewed in Table III. Since the matrix peaks have been discussed above, they will not be addressed here.

There are two major peaks arising from the Pd(II) complex: at m/z = 209.3 and 246.3. These two peaks are emphasized in the inset in Fig. 1a to demonstrate the complex structure of the experimentally obtained peak group, as described in the theoretical presentation of the spectra of the complexes (*cf.* Fig. 2). The latter peak (at m/z = 246.3) is generated by the elimination of one easy-leaving Cl^- from the complex, which leaves the singly-positively charged species; additional loss of neutral HCl from the complex results in the generation of the ion detectable at the lower m/z ratio. Neither significant changes nor additional peaks were detected in the spectra of this complex acquired with DHB matrix after the addi-

tion of TFA (Figs. 3a and 3b). In a previous work, the peaks arising from the Pd(II) complex were not detectable after addition of TFA to the matrix solution.[19] It seems that the conditions that were previously applied were different and that the concentration of the Pd(II) complex in the previous work was sufficiently high to lead to saturation of the detector. In this work, 10-fold lower concentration of complex was tested, which seemed to result in well detectable peaks.

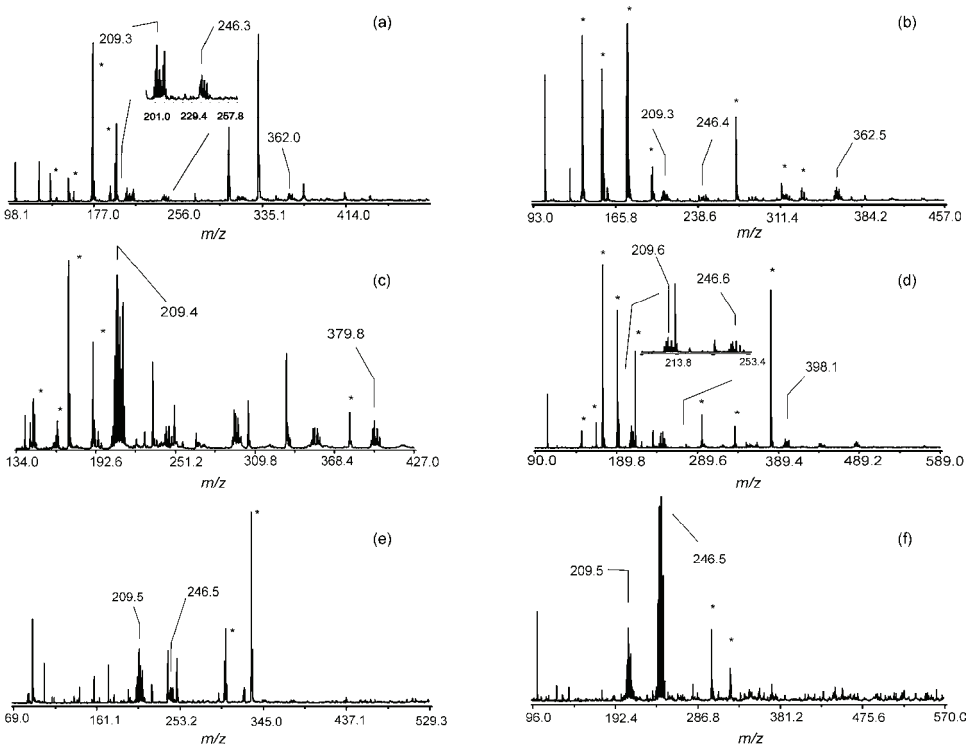

Fig. 3. Positive ion MALDI-TOF mass spectra of the Pd complex acquired with DHB (a and b), CHCA (c and d) and quercetin (e and f). Spectra in a, c and e were acquired without TFA, whereas a small amount of TFA was added to the matrix solutions for the spectra given in b, d and f. The insets in the traces present the expanded mass region from $m/z \approx 200$ up to 260.

When CHCA was used as matrix, only one high-intensity peak arising from the Pd complex at m/z=209.4 was detectable in the MALDI-TOF mass spectra of [Pd(dien)Cl]Cl (Fig. 3c). After the TFA addition, both peaks arising from the complex could be detected, but at much lower intensity compared to the peak obtained without TFA. Similar spectra were obtained also in a previous work and it is important to indicate that this behavior and formation of unusual clusters with the matrix was the motivation to test new matrices for the reliable MALDI-TOF MS analysis of transition metal complexes.

TABLE III. Peaks detected in the positive ion MALDI-TOF mass spectra of the Pd and Ru complexes. The corresponding spectra are given in Figs. 3 and 4; "M" corresponds to the molecule; Q: quercetin

Matrix	*m/z*	Peak assignment
	[Pd(dien)Cl]Cl	
2,5-DHB	209.4	M – HCl – Cl^-
α-CHCA	246.6	M – Cl^-
Q		
Q		
2,5-DHB (TFA)	362.5	M – Cl^- – HCl + 2,5-DHB
α-CHCA	398.1	M + Cl^- – HCl + α-CHCA
	397.8	Not assigned
	$[Ru(en)_2Cl_2]Cl$	
2,5-DHB	193.5	Not assigned
2,5-DHB	292.6	M – Cl^-
α-CHCA		
Q		
2,5-DHB	373.4	M – H^+ + $2Na^+$
2,5-DHB	412.6	n.a.

As will be shown in this section, quercetin with the addition of TFA appeared to be the most suitable matrix for the analysis of [Pd(dien)Cl]Cl. The two peaks arising from the complex were also detected in the spectra acquired with quercetin (Fig. 3e). After the addition of TFA, the intensity of these peaks arising from the Pd(II) complex strongly increased in comparison to the matrix peaks. This might be surprising, since the addition of TFA leads most probably to the fragmentation of quercetin induced by the laser irradiation, as observed in the LDI-TOF mass spectra of quercetin (*cf.* Fig. 1f). On the other hand, it is possible that the amount of quercetin, which is still able to absorb the UV light and to assist desorption and the ionization process of the analyte favored by TFA, is quite sufficient and results in higher peak intensities compared to the spectra obtained without TFA.

MALDI-TOF MS Analysis of $[Ru(en)_2Cl_2]Cl$ complex

The positive ion MALDI-TOF mass spectra of $[Ru(en)_2Cl_2]Cl$ acquired with DHB (Figs. 4a and 4b), CHCA (Figs. 4c and 4d) and quercetin as matrices (Figs. 4e and 4f) are shown in Fig. 4. The spectra in Figs. 4a, 4c and 4e were acquired without TFA, whereas for the spectra presented in other traces given in Fig. 4, a small amount of TFA was added.

A peak arising from the Ru(III) complex is detectable at *m/z* = 292.5 and it is generated by the lost of Cl^- from the complex, resulting in a single positively charged ion. The isotopic peak distribution of this positive ion can be observed in the inset to spectrum in Fig. 4a. There are also other peaks which might arise

from Ru, judging by the characteristic spectra pattern (at *m/z* = 193.5, 373.4 and 412.6, Fig. 4b), but their identity remains so far unknown.

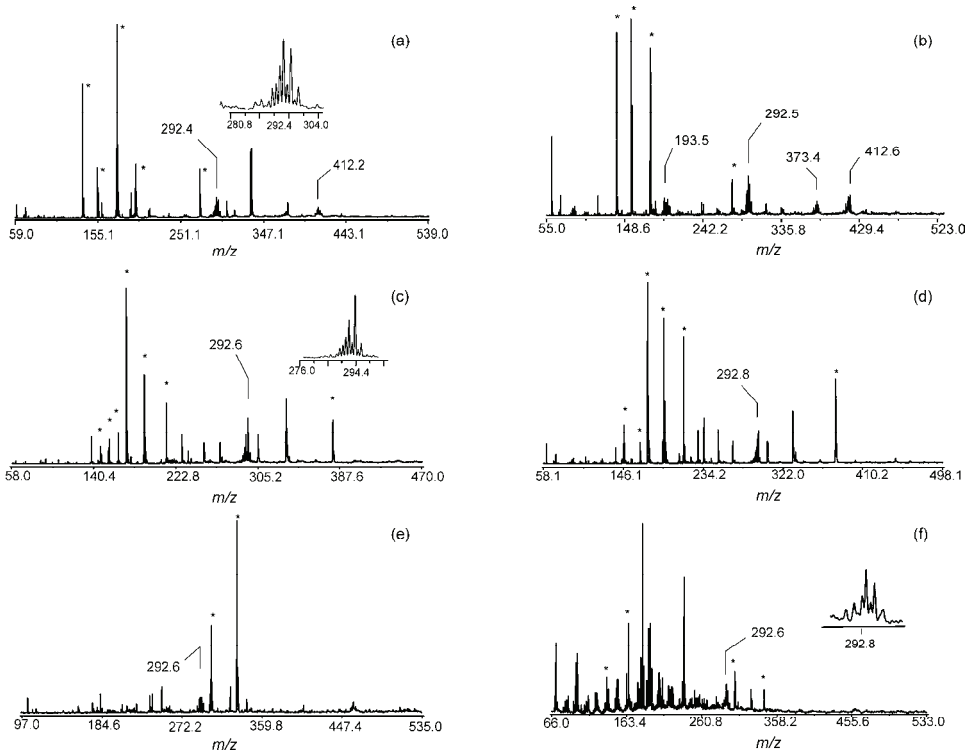

Fig. 4. MALDI-TOF mass spectra of the Ru(III) complex acquired with DHB (a and b), CHCA (c and d) and quercetin (e and f) matrices. The matrix solutions for the spectra in a, c and e were prepared without TFA, whereas for the spectra b, d and f, 0.1 % TFA was added to the matrix solutions. The insets in the figure represent the expanded regions of the *m/z* ratio where characteristic peaks arising from the Ru(III) complex are detected.

Effect of the laser intensity on the S/N *ratio*

In the last part of the experiments, the dependence of the *S*/*N* ratio of peaks arising from the Pd and Ru complexes on the applied laser intensity was tested and the changes in the S/N in relationship with the matrix used and the presence of TFA were compared.

[Pd(dien)Cl]Cl. The dependence of the *S*/*N* ratio of the Pd(II) complex peak at *m/z* = 209.4 on the applied laser intensity when the positive ion MALDI-TOF mass spectra of this transition metal complex were acquired with the assistance of DHB (Fig. 5a), CHCA (Fig. 5b) and quercetin (Fig. 5c) are presented in Fig. 5. For some of the measurements, a small amount TFA was added to the matrix

solution. The laser intensity, expressed in internal, arbitrary units, a.u, was changed gradually and varied from 1500 to 2300 a.u.

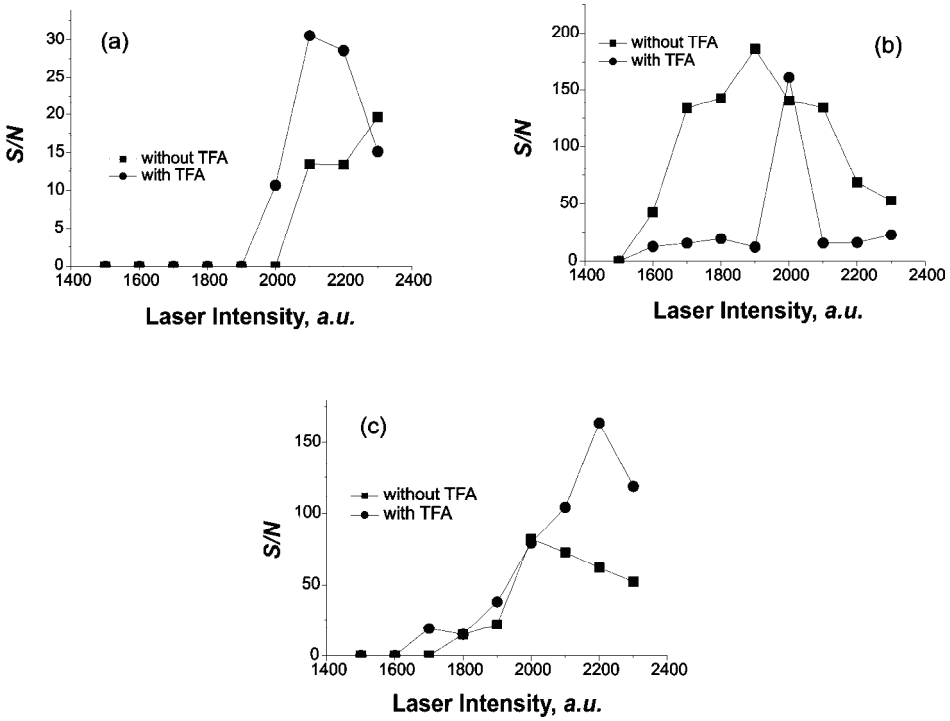

Fig. 5. *S*/*N* ratio of the peak arising from the positive ion MALDI-TOF mass spectra of the Pd(II) complex at *m*/*z* = 209.4 acquired either with DHB (a), CHCA (b) or quercetin (c) as matrices. All the spectra were recorded with or without TFA as indicated in the graphs. The presented results are an average of three independent measurements.

When DHB was used as the matrix, the first signal at *m*/*z* = 209.4 appeared at about 2100 a.u. without TFA and at about 2000 in the presence of TFA. Subsequently, the *S*/*N* ratio of the selected peak increased and reached the maximum already at about 2100 with TFA, whereas in the absence of TFA, this maximum was shifted towards higher laser intensities. Moreover, it seems that the maximum of the *S*/*N* ratio was not reached in the laser intensity range set for testing (Fig. 5a). Unfortunately, due to instrument limitations, a further increase in the laser intensity was not possible.

In the case of the CHCA matrix (Fig. 5b), the palladium peak appeared at much lower laser intensity (already at 1500 a.u.) without TFA, whereas the *S*/*N* ratio for this peak was much lower when TFA was added to the matrix solution. This might be explained by the ionization properties of CHCA: in the presence of

TFA, the ionization of the matrix itself is enhanced, and it might be that the matrix peaks suppressed the peak of interest.

The peak arising from the Pd complex was also detectable with the assistance of quercetin as the matrix (Fig. 5c) and had its maximum intensity at 2000 a.u. in the absence of TFA, whereas its maximum was shifted towards higher laser intensity in the presence of TFA. This might be explained by the increased fragmentation of quercetin induced by the laser in the presence of TFA, which results most probably in a somewhat lower quercetin concentration for the matrix function.

[Ru(en)$_2$Cl$_2$]Cl. In the case of the Ru(III) complex used in this study, the peak at *m/z* = 292.6 was selected for the analysis of the effect of the laser intensity on the *S*/*N* ratio in relationship to the matrix used. The results are shown in Fig. 6; in Fig. 6a DHB was used as the matrix, in Fig. 6b CHCA and in Fig. 6c quercetin was tested.

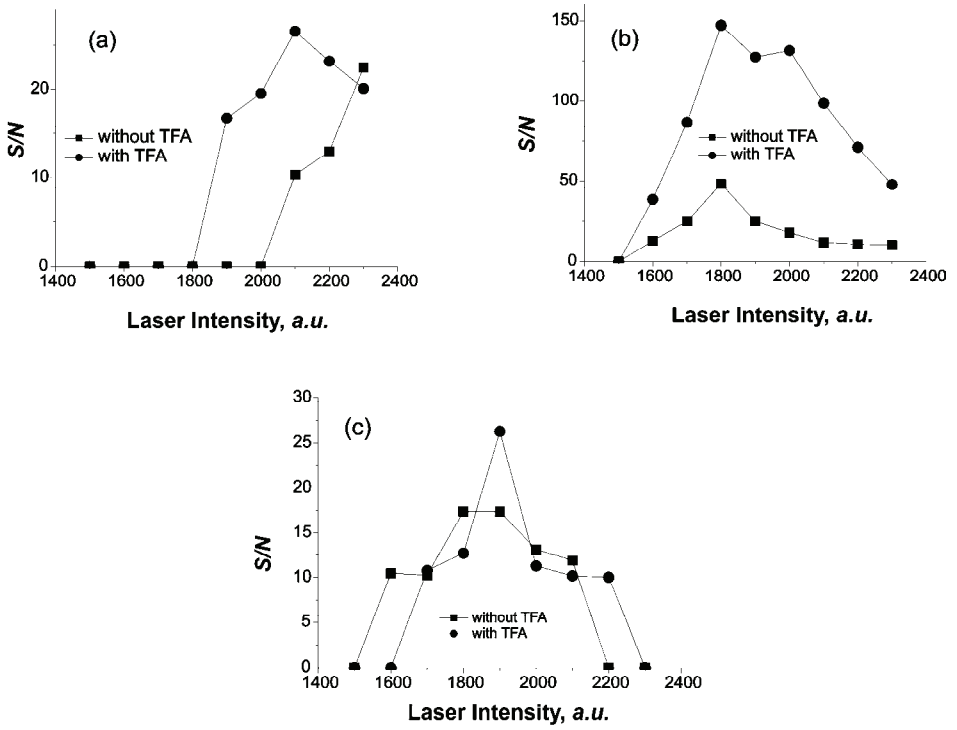

Fig. 6. *S*/*N* ratio of the peak arising from the positive ion MALDI-TOF mass spectra of the Ru(III) complex at *m/z* = 292.6 acquired either with the DHB (a), CHCA (b), or quercetin (c) as matrices. All the spectra were recorded with or without TFA as indicated in the graphs. The presented results are an average of three independent measurements.

In a similar manner to the Pd(II) complex, the addition of TFA to the DHB matrix solution results in a slight shift of the maximum *S*/*N* ratio towards lower applied laser intensities in comparison to DHB without TFA. In the latter case, the maximum *S*/*N* ratio was most probably not achieved, due to instrumental limitations.

When CHCA was used as the matrix, a difference was observed in the pattern of the *S*/*N* ratio of the peak arising from Ru(III) complex compared to that of the Pd(II) complex, thus with addition of TFA, the *S*/*N* ratio was in this case much higher compared to the matrix prepared without TFA (Fig. 6b). The maximum *S*/*N* ratio was achieved at about 1800 a.u., irrespective of the presence of TFA. This different behavior in comparison to the Pd(II) complex might be explained by the detectability of the Ru(III) complex also without matrix[12] (and unpublished observations), which also contributes to the high signal intensity in the presence of the matrix.

When quercetin was used as the matrix for the analysis of the Ru(III) complex, addition of TFA resulted in a shift of the *S*/*N* ratio towards somewhat higher laser intensities required for peak to be detectable in the MALDI-TOF mass spectra of the Ru(III) complex. On the other hand, the maximum *S*/*N* ratio was measured at about 1900 a.u. for both the spectra recorded with and without TFA.

CONCLUSIONS

In summary, matrices used for MALDI-TOF MS analysis of the studied Pd(II) and Ru(III) complexes exhibited differences in their behavior with respect to the quality of the obtained positive ion mode mass spectra. In general, quercetin gave much simpler spectra, resulting in the easy detection and analysis of the complexes. The generation of clusters with DHB and CHCA matrices complicated the spectra of the transition metal complexes, whereas it seems that quercetin stabilized both the Pd(II) and Ru(III) complexes for their detection by MALDI-TOF MS. The addition of TFA to the matrix solution did not significantly affect the quality of the spectra, but affected the intensity of the signals arising from the complexes. Taken together, the results presented in this study once more confirmed the necessity for the establishment of reliable conditions for the analysis of the novel metallo-drugs by MALDI-TOF MS and for potential investigations of their interaction with various classes of biomolecules by this method.

ABBREVIATIONS

CHCA – α-cyano-hydroxycinnamic acid; DHB – 2,5-dihydroxybenzoic acid; ESI – electrospray ionization; FAB – fast atom bombardment; LDI – laser desorption and ionization; MALDI-TOF MS – matrix-assisted laser desorption and ionization time-of-flight mass spectrometry; MS – mass spectrometry; SA – synapinic acid; TFA – trifluoroacetic acid.

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И З В О Д

ПОРЕЂЕЊЕ MALDI-TOF МАСЕНИХ СПЕКТАРА [PdCl(dien)]Cl И $[Ru(en)_2Cl_2]Cl$ КОМПЛЕКСА СНИМЉЕНИХ УЗ ПОМОЋ РАЗЛИЧИТИХ МАТРИЦА

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У овом раду су испитивани експериментални услови за *matrix-assisted laser desorption and ionization time-of-flight* (MALDI-TOF) масеноспектрометријску детекцију и анализу [PdCl(dien)]Cl и $[RuCl_2(en)]Cl$ комплекса. Спектри ових једињења су снимљени уз помоћ традиционалних матрица – 2,5-дихидроксибензоеве киселине и α-цијанохидроксициметне киселине – и уз помоћ кверцетина. Најједноставнији спектри се добијају уз помоћ кверцетина као матрице, док се са осталим матрицама појављују сигнали који потичу од јона формираних додатком молекула матрице или од производа фрагментације молекула. Додатак трифлуоросирћетне киселине (TFA) не компликује спектра Pd(II) и Ru(III) уколико се користе традиционалне матрице, док су спектри Pd(II) комплекса добијени уз помоћ кверцетина и уз додатак TFA једноставнији за интерпретацију. С друге стране, у MALDI-TOF маселим спектрима Ru(III) комплекса се детектују додатни сигнали након додатка TFA. На крају, у овом раду је показана неопходност проналажења услова за сваку комбинацију узорак/матрица, као и значајне разлике у квалитету, односно у броју сигнала у MALDI-TOF маселим спектрима комплекса прелазних метала када се користе различите матрице за снимање.

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