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Proceedings

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**The Conference is dedicated to the  
100th Anniversary of the academician Pavle Savić birthday  
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# MALDI-TOF MS CHARACTERIZATION OF TRANSITION METAL COMPLEXES

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## Abstract

In this work, we have analyzed the positive ion MALDI-TOF mass spectra of cationic complexes [PdCl(*dien*)]Cl and [Ru(*en*)<sub>2</sub>Cl<sub>2</sub>]Cl acquired with different matrices: 2,5-dihydroxybenzoic acid (DHB),  $\alpha$ -cyano hydroxycinnamic acid (CHCA) and quercetin. The necessity to test several matrix/analyte combinations for reliable identification and characterization of metallo-drugs is emphasized in this work.

## Introduction

Several methods can be used for the analysis and characterization of new metallo-drugs and for monitoring of their interaction with biomolecules. Among them, matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS) seems to be promising due to its capability of analysis of both, transition metal complexes and biomolecules. [1]

Choice of the matrix for the MALDI-TOF MS is an important issue since the matrices used for MALDI-TOF mass spectrometric analysis of transition metals complexes exhibit certain drawbacks, as we have recently described, [2-4] and flavonoids appear as good candidates for this purpose.

Main aim of this work was to analyse the spectra of two cationic complexes ([PdCl(*dien*)]Cl and [Ru(*en*)<sub>2</sub>Cl<sub>2</sub>]Cl) obtained with the assistance of traditional matrices (DHB and CHCA) and with selected flavonoid, quercetin. Moreover, the positive ion MALDI-TOF mass spectra in more acidic environment — addition of trifluoroacetic acid (TFA) to the matrix solution usually applied for biomolecules — were analyzed. [1]

## Experimental

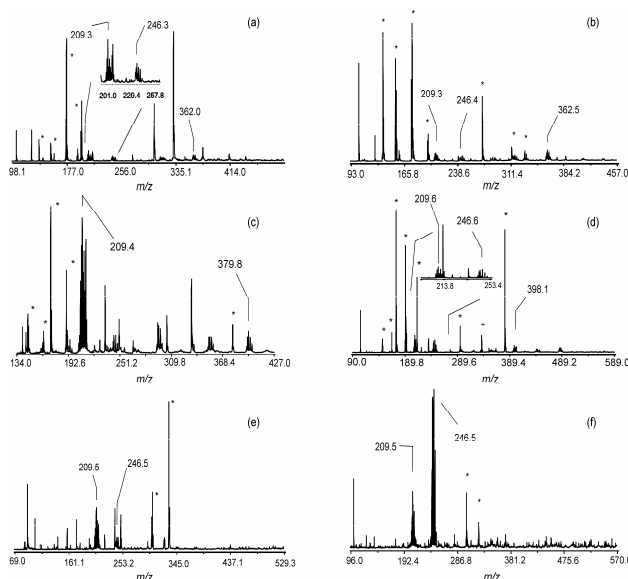
Paladium(II) and ruthenium(III) complexes: [Pd(*dien*)Cl]Cl (diethylenetriamine paladium(II) chloride) (*Mr*=280.5) and [Ru(*en*)<sub>2</sub>Cl<sub>2</sub>]Cl (dichlorido (ethylenediimine)ruthenium(III) chloride) (*Mr*=327.6) were synthesised as described in the literature. [5,6] Other chemicals were purchased from Sigma Aldrich Chemie GmbH (München, Germany). Metal complexes were dissolved in a combination of methanol/physiological solution (10<sup>-3</sup>M). Matrices (2,5-DHB and  $\alpha$ -CHCA) were prepared prior to use. MALDI-TOF mass spectra were acquired on a Voyager Biospectrometry DE Pro Workstation (Perseptive Biosystems, Framingham, MA,

USA). The spectra were acquired without a low mass gate and under delayed extraction conditions in the reflector mode. [2-4]

## Results and discussion

All peaks detected in the MALDI-TOF mass spectra of selected transition metal complexes with their identity are listed in Table 1.

The positive ion MALDI-TOF mass spectra of  $[\text{Pd}(\text{dien})\text{Cl}]\text{Cl}$  acquired with various matrices with or without TFA are given in Fig 1. Two peaks are emphasized in the inset in Fig. 1a to demonstrate the complex structure of the peak group. Neither significant changes nor additional peaks have been detected in the spectra of this complex acquired with DHB matrix after addition of TFA (Figs. 1a and 1b). When CHCA was used as matrix, only one peak (at  $m/z=209.4$ ) arising from the Pd complex with high intensity was detectable (Fig. 1c). After the TFA addition, both peaks arising from the complex could be detected, but with much lower intensity compared to the peak obtained without TFA. Ions generated from the transition metal complex and used matrices were detected with both traditional matrices (Table 1 and Fig. 1). This was also observed in our previous work. [3]



**Fig. 1.** Positive ion MALDI-TOF mass spectra of Pd complex acquired with DHB (a and b), CHCA (c and d) and quercetin (e and f). Spectra in a, c, and e are acquired without TFA, whereas TFA was added to the matrix solutions for the spectra given in b, d and f. Inset in traces a and d presents expanded mass region from  $m/z \sim 200$  to 260.

Quercetin with the addition of TFA appeared to be the most suitable matrix for the analysis of  $[\text{Pd}(\text{dien})\text{Cl}]\text{Cl}$ . The two peaks arising from the complex have also been detected in the spectra acquired with quercetin (Fig. 1e). After addition of TFA the intensity of these peaks arising from the Pd(II) complex strongly increases in comparison to the matrix peaks.

MALDI-TOF mass spectra of  $[\text{Ru}(\text{en})_2\text{Cl}_2]\text{Cl}$  yield only one peak arising from this complex (at  $m/z=292.6$ ). Although quercetin generates simple pattern, addition of TFA to this matrix results in the almost complete suppression of the analyte peaks (data not shown).

[PdCl(dien)]Cl		
Matrix	m/z	Peak assignment
2,5 – DHB ; $\alpha$ – CHCA; Q	104.3	$[N_3C_4H_{14}]^+$
	209.4	$[M - HCl - Cl]^+$
	246.6	$[M - Cl]^+$
2,5 – DHB (TFA)	362.5	$[M - Cl - HCl + 2,5-DHB]^+$
$\alpha$ – CHCA	398.1	$[M + Cl^- - HCl + \alpha-CHCA]^+$
	485.1	n.a.*
[Ru(en) <sub>2</sub> Cl <sub>2</sub> ]Cl		
2,5 – DHB	193.5	n.a.*
2,5 – DHB	292.6	$[M - Cl]^+$
$\alpha$ – CHCA		
Q		
2,5 – DHB	373.4	$[M - H^+ + 2Na^+]^+$
2,5 – DHB	412.6	n.a.*

**Table 1.** 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. \*, „n.a.“: not assigned

In all spectra recorded, peak at  $m/z=104.3$  (ethylenediamine,  $[N_3C_4H_{14}]^+$ ) arises. Although not quantitatively determined, it seems that its intensity increases after addition of TFA to the matrix solution (Figs. 1b, 1d and 1f),

indicating that the TFA might enhance the process of the complex degradation.

## Conclusion

Matrices used for MALDI-TOF MS analysis of transition metal complexes exhibited the differences in their behavior with respect to the quality of the positive ion mode MALDI-TOF mass spectra of Pd(II) and Ru(III) complexes used in this study. In general, quercetin gives much simpler spectra, resulting in the easy detection and analysis of the complexes. The generation of clusters with DHB and CHCA matrices complicates the spectra of transition metal complexes, whereas it seems that quercetin stabilizes both Pd(II) and Ru(III) complexes for their detection by MALDI-TOF MS. Taken together, results presented in this study once more point out the necessity to establish reliable conditions for the analysis of the novel metallo-drugs by MALDI-TOF MS and for potential investigation of their interaction with various classes of biomolecules by this method.

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