Solvent-free MALDI Mass Spectrometry for the Analysis of Metallosupramolecular Complexes

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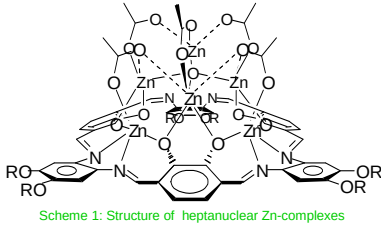
Objectives

➢Comparing the solvent-free and solvent-based MALDI mass spectrometry for the analysis of heptametallic bowl-shaped complexes. The complex includes six acetate ligands.



Scheme 1: Structure of heptanuclear Zn-complexes ($R=C_2H_5$, C_5H_{11}, C_6H_{13})

Methods

➢MALDI-MS experiments were carried out on Bruker Biflex MALDI-TOF using both linear and reflectron modes.

➢Heptanuclear Zn-complexes were prepared and characterized by X-ray crystallography[1].

➢Various matrices including 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB), dithranol and 2-amino-5-nitropyridine (ANP) were tested.

➢Solvent-free MALDI sample preparation was based on mini-ball method[2,3]. 1 mm steel ball was used and grinding time was about 1 minute.

➢Solvent-based MALDI sample was prepared with dried-droplet method.

Results and Discussion

Direct laser desorption/ionization (LDI)

➢LDI failed to show molecular ions and a big unresolved lump around m/z 3000 was observed for three heptanuclear Zn complexes with different peripheral alkoxy chains (Data not shown here). Fragment ions observed in LDI are the same as those with MALDI (see below).

Solvent-free MALDI

➢Molar ratio of analyte to matrix is in the range of 10 to 50. Laser power required is lower than with solvent-based MALDI.

➢MALDI with DCTB matrix formed molecular ion (peak A) as well as fragment ions (peak B, C and E) (Table 1, Fig. 1). Although peak B due to loss of one acetate is always stronger, molecular ion is clearly seen (Fig. 2). Another stable ion is formed due to the loss of three acetates and Zn (peak E).

➢Peak D is broad and observed only in reflectron mode, not in linear mode, suggesting the formation of metastable ions (Fig. 1).

Table 1: MALDI-MS Data for heptanuclear Zn complexes with different peripheral alkoxy chains with DCTB as matrix (listed masses correspond to the most abundant isotopic peaks)

R	C_2H_5	C_5H_{11}	C_6H_{13}	Ion Assignment
A	1801	2053	2137	M
B	1741	1995	2078	M-OAc
C	1616	1872	1952	M-Zn-2OAc
D	1587	1841	1925	
E	1557	1811	1895	M-Zn-3OAc

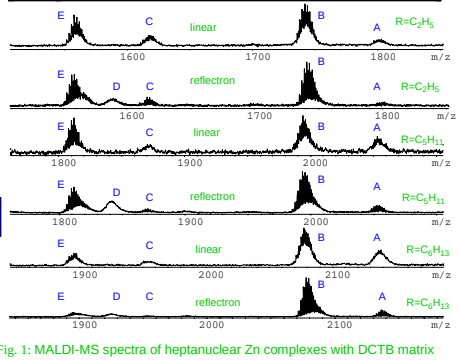


Fig. 1: MALDI-MS spectra of heptanuclear Zn complexes with DCTB matrix

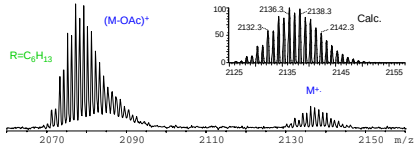


Fig. 2: MALDI-MS spectra of heptanuclear Zn complex with DCTB ($R=C_6H_{13}$). Inset is the calculated isotope pattern of $C_{80}H_{114}N_6O_{25}Zn_7$.

Solvent-based MALDI

➢Similar results are observed with solvent-based MALDI.

➢Molecular ions are observed only with DCTB (peak A in Fig. 3 and 4).

➢Dithranol as matrix failed to give molecular ions. Observed ions are summarized in Table 2.

➢Matrix displacement ions are formed (peak X, Y and Z) in Table 2 and Fig. 5). Each dithranol replaces two acetates. Similar matrix displacement were also observed with ANP and each ANP replaces one acetate (data not shown here).

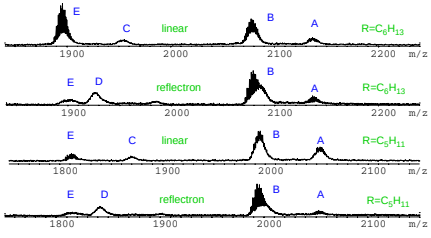


Fig. 3: MALDI-MS spectra of heptanuclear Zn complex with DCTB matrix.

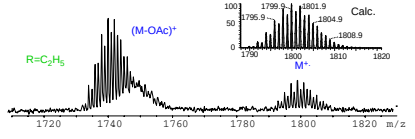


Fig. 4: MALDI-MS spectra of heptanuclear Zn complex ($R=C_2H_5$) with DCTB. Inset is the calculated isotope pattern of $C_{68}H_{86}N_6O_{25}Zn_7$.

Table 2: MALDI-MS Data for heptanuclear Zn complexes with different peripheral alkoxy chains with dithranol as matrix (listed masses correspond to the most abundant isotopic peaks)

R	C_2H_5	C_5H_{11}	C_6H_{13}	Ion Assignment
X	1955	2205	2289	M-5OAc+2Mat
Y	1849	2099	2183	M-3OAc+Mat
B	1741	1995	2077	M-OAc
Z	1663	1916	2002	M-Zn-5OAc+Mat
D	1587	1841	1925	
E	1557	1811	1895	M-Zn-3OAc

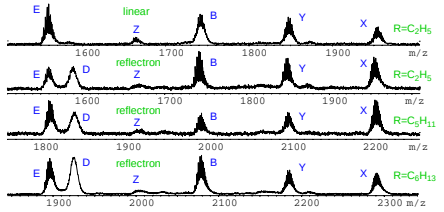


Fig. 5: MALDI-MS spectra of heptanuclear Zn complex with dithranol

Conclusions

➢Solvent-free MALDI generated similar results as solvent-based MALDI for heptanuclear Zn complexes.

➢Molecular ion of heptanuclear Zn complex was only observed with DCTB as matrix.

➢Matrix adducts were formed with dithranol and ANP.

References

1. Gallant, A. J.; Chong, J. H.; MacLachlan, M. J., *Inorg. Chem.*, 2006, 45, 5248-5250.
2. Hanton, S. D.; Parees, D. M., *J. Am Soc. Mass Spectrom*, 2005, 16, 90-93.
3. Trimpin, S.; Keune, S.; Rader, H. J.; Mullen, K., *J. Am Soc. Mass Spectrom*, 2006, 17, 661-671.

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