

Notes

## Crystal Structure and Electrospray Mass Spectrum of Tris(2,5-dioxopyrrolidin-1-ylmethyl)amine

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A novel N-Mannich base tris(2,5-dioxopyrrolidin-1-ylmethyl)-amine (TDOPMA) was synthesized and its structure was determined by single crystal X-ray diffraction. Unlike NH<sub>3</sub> molecule, three C-N-C bond angles containing the central N atom in the title compound are unequal and about 9° larger than H-N-H angles of NH<sub>3</sub> molecule. Electrospray ionization (ESI) mass spectrometry was applied to the title compound. Its fragments were interpreted and possible fragmentation mechanism was given.

**Keywords** Crystal structure, tris(2,5-dioxopyrrolidin-1-ylmethyl)amine, electrospray mass spectrum, Mannich reaction

### Introduction

More and more attention has been paid to photochromic materials and various types of photochromic compounds have been developed in an attempt to be applied to optical data storage<sup>1,2</sup> and optical switches.<sup>3</sup> A series of organic compounds were synthesized, the lanthanide complexes of which with 1,10-phenanthroline in aqueous solution have photochromic behavior.<sup>4-7</sup> What is more, the lanthanide ion and the ligands are all essential to the photochromism, which is distinguished from the other reported photochromic system.<sup>8-10</sup> In order to extend our research, through Mannich reaction we synthesized the title compound tris(2,5-dioxopyrrolidin-1-ylmethyl)amine and its lanthanide complexes with 1,10-phenanthroline were formed in aqueous solution, resulting in photochromic phenomenon.

Mass spectrometry is an attractive technique for determining molecular weight and molecular fragmentation. However, it was limited to low molecular weight compounds that could be readily volatilized. Larger species could not be promoted into the gas phase without substantial degradation and/or fragmentation.<sup>11</sup> Recently, considerable attention has been focused on soft ionization for mass spectrometry. The ESI mass spectrometry developed by John Fenn and co-workers is a technique with which electrolyte ions present in solution can be transferred to the gas phase gently with slight or no fragmentation.<sup>12,13</sup> The characteristic feature of ESI that distinguishes it from other ionization techniques is that it generally imparts multiple charges to larger analyte molecules, and the extent of multiple charging increases in near proportion to molecular weight. The resulting highly charged molecular ions are thus within the *m/z* range where conventional mass spectrometers function fairly well.<sup>11</sup> The ions generated by ESI usually carry multiple protons if they carry positive charges, and the ions observed in the mass spectrum in many cases reflect the species present in the solution.<sup>14</sup>

In this paper, we report the crystal structure and the ESI mass spectrum of the title compound.

### Experimental

All reagents used are of analytical grade.

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### Preparation of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine

*N, N*-Bis(2,5-dioxopyrrolidin-1-ylmethyl)glycine (DOPMG) was prepared as described in literature.<sup>6</sup> DOPMG (2 g) was dissolved in 5 mL of distilled water, adjusting pH = 7 with 1 mol/L NaOH solution. The mixture was heated at 80°C with stirring for 20 h. A clear solution with pH = 5.7 was obtained. Two months later, crystals suitable for X-ray analysis were obtained at room temperature. Anal. C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>. Calcd: C, 51.42; H, 5.18; N, 16.00. Found: C, 51.08; H, 5.07; N, 15.51.

### X-ray crystallographic determination

A colorless prismatic crystal of the title compound

was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo K $\alpha$  ( $\lambda = 0.071069$  nm) radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 21 carefully centered reflections. The data were collected at a temperature of  $20 \pm 1$  °C using the  $\omega$ - $2\theta$  scan technique. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods<sup>15</sup> and expanded using Fourier techniques.<sup>16</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan<sup>17</sup> crystallographic software package of Molecular Structure Corporation. The crystal data and experimental details are summarized in Table 1.

**Table 1** Crystal data and experimental details

Formula weight	350.33
Crystal dimensions	0.20 × 0.20 × 0.30 mm
Crystal system	triclinic
Lattice parameters	$a = 0.9417(4)$ nm, $\alpha = 102.73(3)^\circ$ $b = 1.0618(4)$ nm, $\beta = 98.11(3)^\circ$ $c = 0.9072(2)$ nm, $\gamma = 65.64(3)^\circ$ $V = 0.804.8(5)$ nm <sup>3</sup>
Space group	$P\bar{1}$
<i>Z</i>	2
Density (calculated)	1.446 g/cm <sup>3</sup>
<i>F</i> (000)	368.00
Absorption coefficient	1.13 cm <sup>-1</sup>
Wavelength (Mo K $\alpha$ )	0.071069 nm
Temperature	20.0°C
$2\theta_{\max}$	55.0°
Reflections collected	3921
Unique reflections	3695 ( $R_{\text{int}} = 0.008$ )
Refinement method	Full-matrix least-squares
Index ranges	$0 \leq h \leq 12$ , $-11 \leq k \leq 13$ , $-11 \leq l \leq 11$
Data/restraints/parameters	3695/0/227
Goodness of fit indicator	1.80
Largest diff. peak and hole	290 e/nm <sup>3</sup> and $-190$ e/nm <sup>3</sup>

### Determination of electrospray mass spectra

Sample was prepared by dissolving tris(2,5-dioxopyrrolidin-1-ylmethyl)amine in distilled water at a concentration of 1 mg/mL. 1  $\mu$ L of such solution was loaded into the injection valve of the LCQ (Finnigan Mat) unit

and then injected into the mobile phase solution (methanol:H<sub>2</sub>O = 1:1, *V/V*) and carried through the electrospray interface into the mass analyzer at a rate of 200  $\mu$ L/min. The employed voltage at the electrospray needles was 4.5 kV and the capillary was heated to 200°C. A maximum ion injection time of 200 ms along

with 10 scans was set. Experiments were performed in the positive ion mode. The ESI mass spectrum was recorded in the range of 150–1000. Predicted isotope distribution patterns for each of observed species were calculated by Isopro 3.0 program.

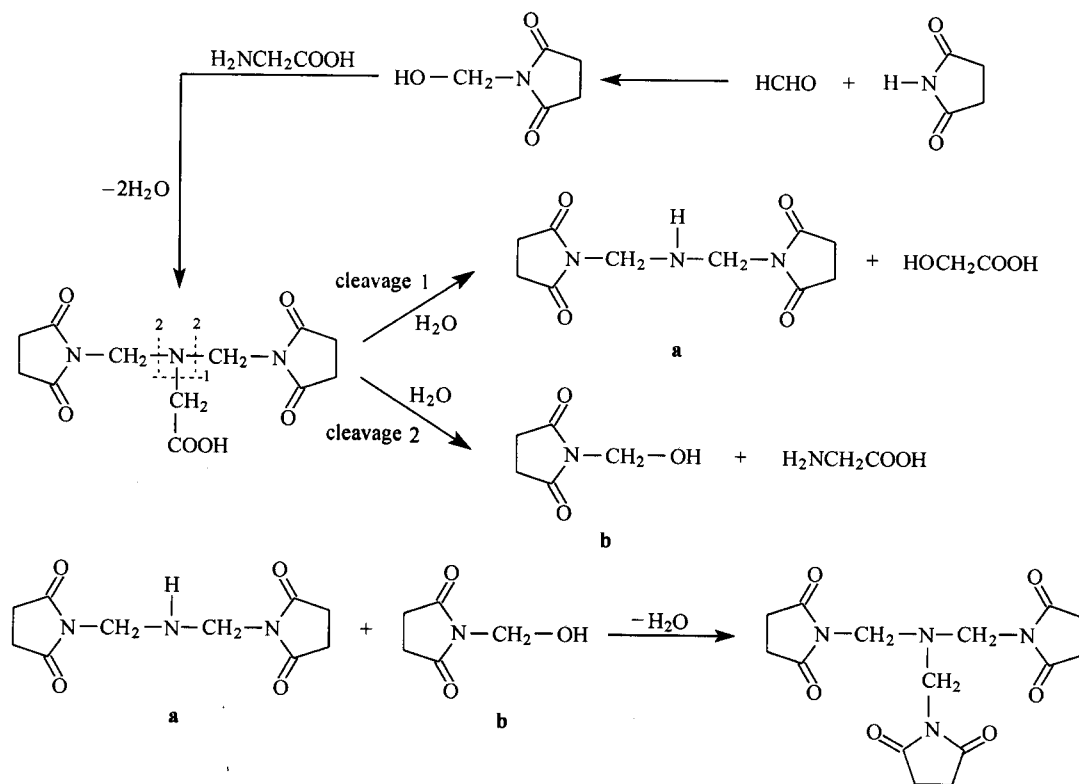
## Result and discussion

### Formation of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine

The synthesis of DOPMG was accomplished through a typical Mannich reaction. According to the theory of

Zinner and Herbig,<sup>18</sup> firstly, the N-H acid, succinimide, condenses with HCHO forming the intermediate *N*-hydroxymethyl succinimide. Then the intermediate reacts with primary amine, glycine, to produce *N*-Mannich base DOPMG by dehydration. However, Mannich base is ready to undergo deamination reaction<sup>19</sup> which can be considered as the reverse reaction of Mannich reaction. In the case of DOPMG, the cleavage paths shown in Scheme 1 can occur, which results in a secondary amine, bis(2,5-dioxopyrrolidin-1-ylmethyl)amine (**a**) and an *N*-hydroxymethyl succinimide (**b**). Then compound **a** reacts with **b** by dehydration to give the product tris(2,5-dioxopyrrolidin-1-ylmethyl)amine.

**Scheme 1** Formation of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine



### Molecular structure of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine

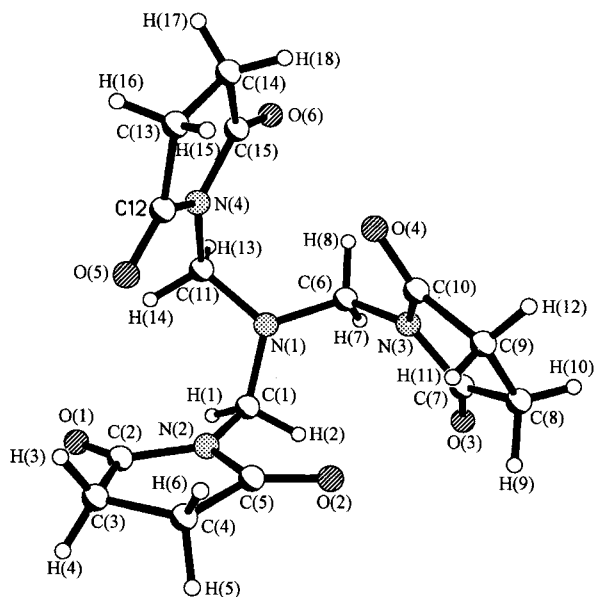
The bond lengths and bond angles of TDOPMA are listed in Tables 2 and 3, respectively. Fig. 1 shows the molecular structure of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine.

The title compound is composed of four parts: a central N(1) atom and three 2,5-dioxopyrrolidin-1-yl-

methyl groups. But not all the corresponding structural data are the same. The central N(1) atom is  $\text{sp}^3$  hybridization. The angles of C(1)-N(1)-C(6), C(1)-N(1)-C(11) and C(6)-N(1)-C(11) are  $116.8^\circ$ ,  $116.3^\circ$  and  $115.8^\circ$ , respectively, which are significantly different from those in the molecule  $\text{NH}_3$  where all the H-N-H angles are  $107^\circ$ . This is because the groups bonded to N(1) are all 2,5-dioxopyrrolidin-1-ylmethyl group which is a bulky group in the title compound.

**Table 2** Bond distances (nm) of TDOPMA

Atom	Atom	Distance	Atom	Atom	Distance
O(1)	C(2)	0.1208(3)	N(3)	C(10)	0.1395(2)
O(2)	C(5)	0.1209(3)	N(4)	C(11)	0.1456(3)
O(3)	C(7)	0.1213(2)	N(4)	C(12)	0.1387(2)
O(4)	C(10)	0.1206(2)	N(4)	C(15)	0.1384(3)
O(5)	C(12)	0.1207(3)	C(2)	C(3)	0.1503(4)
O(6)	C(15)	0.1207(2)	C(3)	C(4)	0.1514(5)
N(1)	C(1)	0.1444(2)	C(4)	C(5)	0.1504(3)
N(1)	C(6)	0.1448(2)	C(7)	C(8)	0.1503(3)
N(1)	C(11)	0.1445(2)	C(8)	C(9)	0.1517(3)
N(2)	C(1)	0.1457(2)	C(9)	C(10)	0.1504(3)
N(2)	C(2)	0.1379(3)	C(12)	C(13)	0.1493(3)
N(2)	C(5)	0.1390(3)	C(13)	C(14)	0.1516(4)
N(3)	C(6)	0.1450(2)	C(14)	C(15)	0.1498(3)
N(3)	C(7)	0.1381(2)			

**Fig. 1** Molecular structure of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine**Table 3** Bond angles ( $^{\circ}$ ) of TDOPMA

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(1)	N(1)	C(6)	116.8(1)	N(2)	C(5)	C(4)	107.5(2)
C(1)	N(1)	C(11)	116.3(1)	N(1)	C(6)	N(3)	110.3(1)
C(6)	N(1)	C(11)	115.8(1)	O(3)	C(7)	N(3)	124.0(2)
C(1)	N(2)	C(2)	123.9(2)	O(3)	C(7)	C(8)	127.9(2)
C(1)	N(2)	C(5)	122.4(2)	N(3)	C(7)	C(8)	108.1(2)
C(2)	N(2)	C(5)	113.6(2)	C(7)	C(8)	C(9)	105.3(1)
C(6)	N(3)	C(7)	124.5(1)	C(8)	C(9)	C(10)	104.9(1)
C(6)	N(3)	C(10)	122.3(1)	O(4)	C(10)	N(3)	123.2(2)
C(7)	N(3)	C(10)	112.9(1)	O(4)	C(10)	C(9)	128.9(2)
C(11)	N(4)	C(12)	122.3(2)	N(3)	C(10)	C(9)	107.9(2)
C(11)	N(4)	C(15)	123.9(2)	N(1)	C(11)	N(4)	111.2(1)
C(12)	N(4)	C(15)	113.1(2)	O(5)	C(12)	N(4)	123.7(2)
N(1)	C(1)	N(2)	111.4(1)	O(5)	C(12)	C(13)	128.7(2)
O(1)	C(2)	N(2)	123.5(2)	N(4)	C(12)	C(13)	107.6(2)
O(1)	C(2)	C(3)	129.0(2)	C(12)	C(13)	C(14)	106.1(2)
N(2)	C(2)	C(3)	107.5(3)	C(13)	C(14)	C(15)	104.8(2)
C(2)	C(3)	C(4)	105.6(2)	O(6)	C(15)	N(4)	123.8(2)
C(3)	C(4)	C(5)	105.3(2)	O(6)	C(15)	C(14)	127.9(2)
O(2)	C(5)	N(2)	123.9(2)	N(4)	C(15)	C(14)	108.3(2)
O(2)	C(5)	C(4)	128.5(2)				

ESI mass spectrum of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine

Fig. 2 gives the full electrospray mass spectrum of

tris(2,5-dioxopyrrolidin-1-ylmethyl)amine. Under the present condition of electrospray ionization, the abundance of ions derived from the cleavage of single bond is weak.<sup>20</sup> The Na<sup>+</sup> and K<sup>+</sup> ions are present in trace

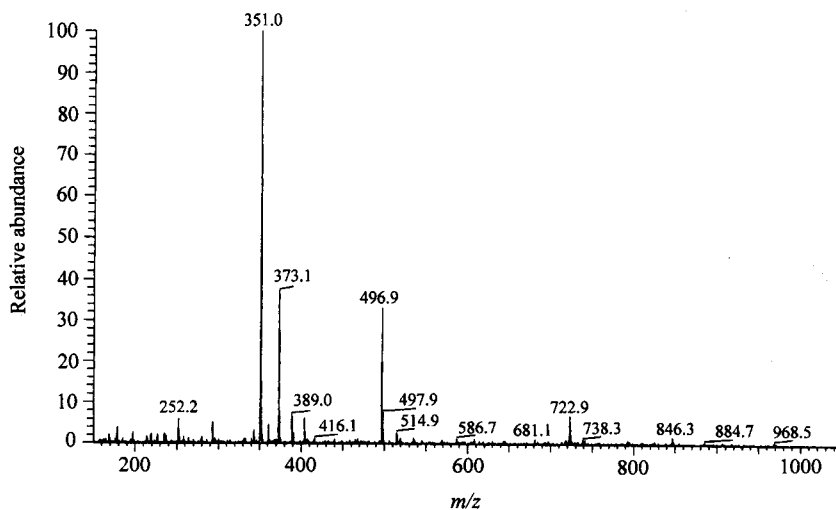


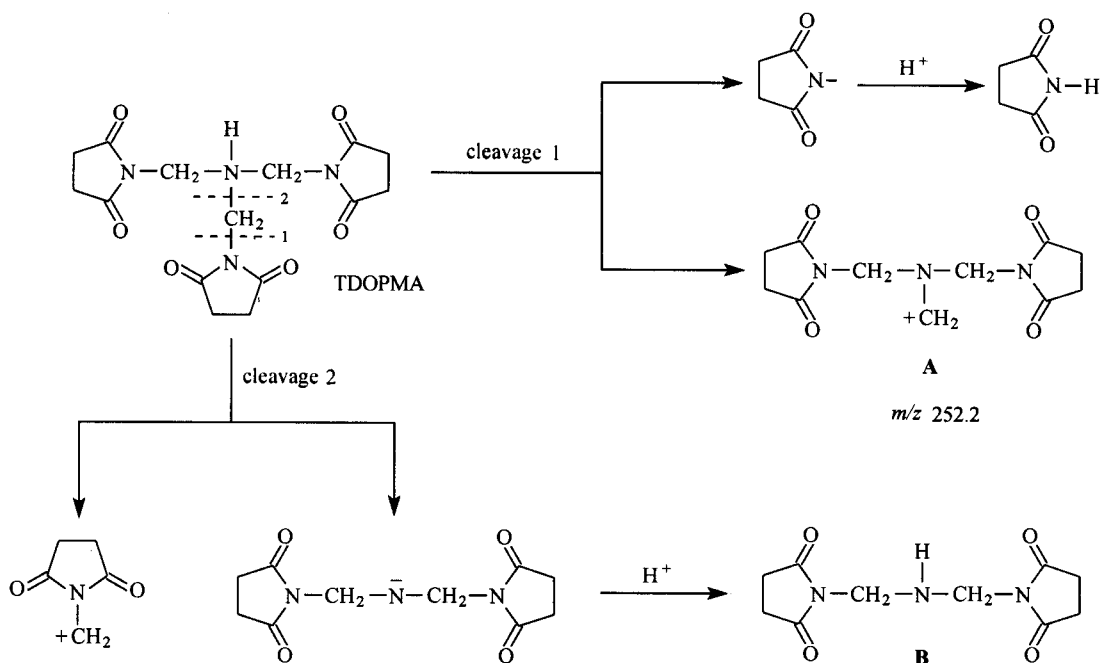
Fig. 2 Full electrospray mass spectrum of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine.

amounts,<sup>21</sup> while the  $H^+$  is in a large amount. The molecule could bind  $H^+$ ,  $Na^+$  and  $K^+$  ions to form adducts  $(TDOPMA + H)^+$ ,  $(TDOPMA + Na)^+$  and  $(TDOPMA + K)^+$ . And it is easy to form  $(2TDOPMA + Na)^+$  ion with a relatively high abundance.<sup>20</sup> It can be seen from Fig. 2 that the most abundant ion is protonated TDOPMAH<sup>+</sup> corresponding to the peak at  $m/z$  351.0. And the peaks at  $m/z$  373.1, 389.0 and 722.9 were obtained from  $(TDOPMA + Na)^+$ ,  $(TDOP-$

$MA + K)^+$  and  $(2TDOPMA + Na)^+$ , respectively. Among the three types of ions, those involving  $Na^+$  are relatively abundant.

As a Mannich base, tris(2,5-dioxopyrrolidin-1-ylmethyl)amine has the common characteristic reaction. It can undergo deamination and deaminomethylation.<sup>19</sup> Therefore, there are two possible cleavage positions for tris(2,5-dioxopyrrolidin-1-ylmethyl)amine (shown in Scheme 2). Cleavage 1 makes the positive A ion at  $m/z$

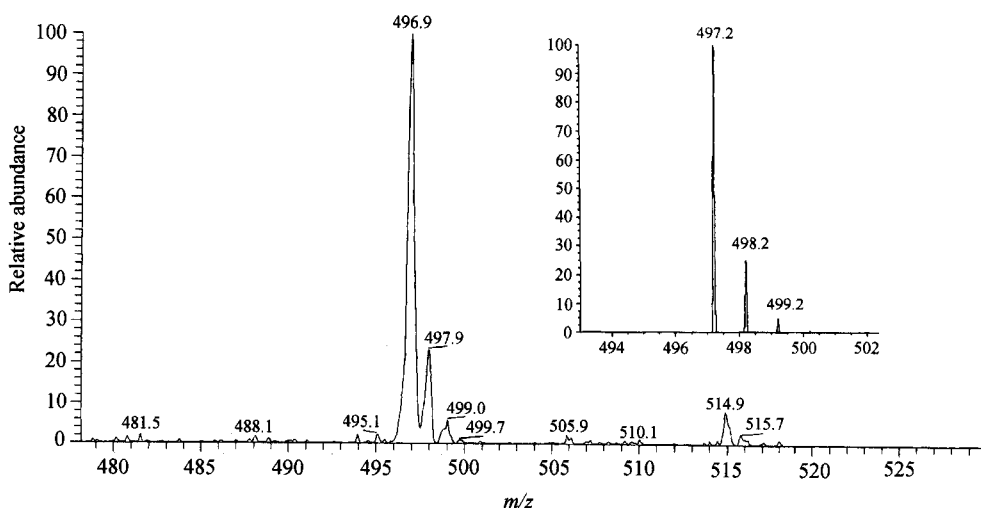
Scheme 2 Fragmentation of tris(2,5-dioxopyrrolidin-1-ylmethyl)amine



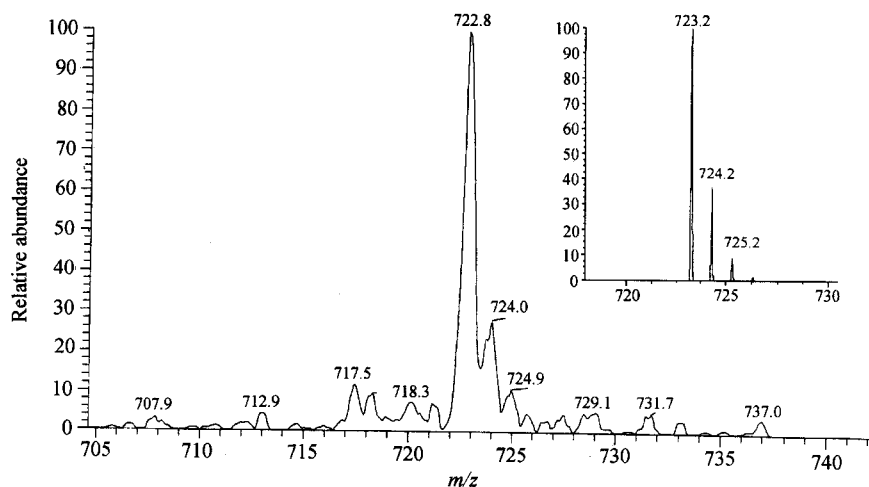
252.2 with a loss of 2,5-dioxopyrrolidinyl. TDOPMA undergoes cleavage 2 leading to an intermediate with a negative ion which may result in product **B** arising from protonation. Two **B** and one H<sub>2</sub>O molecule may be linked to each other through hydrogen bond to form a new molecule. The protonation of the new molecule leads to the ion (2**B** + H<sub>2</sub>O + H<sup>+</sup>) at  $m/z$  496.9. From the expansion of the mass spectrum for the ion at  $m/z$  496.9 (Fig. 3), it can be seen that the difference between the neighboring peaks is 1 Da, which means that it is a singly charged species. The inserted

spectrum in Fig. 3 is its calculated isotopic distribution which conforms to the measured. By the way, in the recorded range of ESI mass spectrum of tris(2,5-dioxopyrrolidin-1-ylmethyl)-amine, there is no multiply charged ion observed. They are all singly charged ones.

For the peak ascribed to (2TDOPMA + Na)<sup>+</sup> at  $m/z$  722.8, the relative abundance and distribution position of the measured isotopic peaks are in good agreement with those calculated as shown in Fig. 4, which confirms the assignment.



**Fig. 3** Expansion of the mass spectrum for the ion at  $m/z$  496.9. The inserted one is calculated isotopic distribution for the ion at  $m/z$  496.9.



**Fig. 4** Expansion of the mass spectrum for the ion at  $m/z$  722.8. The inserted one is calculated isotopic distribution for the ion at  $m/z$  722.8.

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