

## Molecular Structure of Tetrakis(1,2,5–thiadiazolo)–porphyrazinatozinc(II) in Gaseous Phase

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*The molecular structures of gaseous zinc tetrakis(1,2,5-thiadiazolo)porphyrazine, [ZnTTDPz], and 1,2,5-thiadiazole-3,4-dicarbonitrile, C<sub>4</sub>N<sub>4</sub>S, were studied by synchronous gas-phase electron diffraction and mass spectrometric experiment at T=587(5) °C in combination with quantum chemical calculations at theory level B3LYP/cc-pVTZ. The vapour over the sample at the temperature of experiment contained molecules of complex [ZnTTDPz] and 1,2,5-thiadiazole-3,4-dicarbonitrile (C<sub>4</sub>N<sub>4</sub>S) having the molecular symmetry D<sub>4h</sub> and C<sub>2v</sub>, respectively. In contrast to the crystal structure, where Zn atom is displaced out of plane of the coordination moiety, the gaseous molecule [ZnTTDPz] has a planar structure. Geometry of the dinitrile C<sub>4</sub>N<sub>4</sub>S in the gas phase do not differ strongly from that in a crystal.*

**Keywords:** 1,2,5-Thiadiazole, porphyrazine, zinc(II) complex, 1,2,5-thiadiazole-3,4-dicarbonitrile, electron diffraction, DFT, molecular structure.

## Молекулярная структура тетракис(1,2,5–тиадиазоло)–порфиразината цинка(II) в газовой фазе

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*Строение молекул тетракис(1,2,5-тиадиазол)порфиразината цинка, [ZnTTDPz], и 1,2,5-тиадиазол-3,4-дикарбонитрила, C<sub>4</sub>N<sub>4</sub>S, изучено в рамках синхронного электронографического/масс-спектрометрического эксперимента при температуре T=587(5) °C в комбинации с квантово-химическими расчетами методом B3LYP/cc-pVTZ. При температуре эксперимента пар состоял из молекул комплекса [ZnTTDPz] и динитрила C<sub>4</sub>N<sub>4</sub>S, имеющих симметрию D<sub>4h</sub> и C<sub>2v</sub>, соответственно. В противоположность кристаллической структуре, в которой атом цинка выходит из плоскости координационной полости, газообразная молекула [ZnTTDPz] имеет плоское строение. Геометрическое строение молекулы C<sub>4</sub>N<sub>4</sub>S в газовой фазе близко к ее строению в кристалле.*

**Ключевые слова:** 1,2,5-Тиадиазол, порфиразин, комплекс цинка, 1,2,5-тиадиазол-3,4-дикарбонитрил, газовая электронография, молекулярная структура.

Heterocyclic phthalocyanine analogues – porphyrazines with annulated 1,2,5-chalcogenadiazole rings containing peripheral S, Se or Te atoms have received an increasing attention over the last decade,<sup>[1-3]</sup> particularly due to perspectives of their application in organic electronics evidenced for tetrakis(1,2,5-thiadiazolo)porphyrazines.<sup>[4,5]</sup>

X-Ray study<sup>[6]</sup> of the tetrakis(thiadiazolo)porphyrazine and the corresponding metal(II) derivatives ([MTTDPz], M=2H, Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>) showed that a variety of new interunit contacts ( $\pi$ - $\pi$  interactions, S $\cdots$ N electrostatic contacts, M $\cdots$ N coordination bonding) determines the type of molecular packing in different  $\alpha$ ,  $\beta$  and  $\gamma$  solid-state forms. In crystal the structure of the molecules is disturbed due to collective interactions. In the gas phase the structure of the individual molecule can be more strictly correlated with inherent physicochemical properties.

In this work we report for the first time the results of the direct experimental molecular structural investigation of gaseous zinc(II) tetrakis(1,2,5-thiadiazolo)porphyrazine, [ZnTTDPz], by synchronous gas-phase electron diffraction (GED) and mass spectrometric experiment in combination with quantum chemical DFT calculations (B3LYP/cc-pVTZ level). Previously the DFT optimization of [ZnTTDPz] molecule was performed using BP86/TZ2P basis set.<sup>[7]</sup>

The electron diffraction patterns and the mass spectra were recorded simultaneously using a combined GED/MS unit based on EMR-100 and APDM-1 devices.<sup>[8,9]</sup> The sample of [ZnTTDPz] synthesized as described previously<sup>[10]</sup> was evaporated from a molybdenum effusion cell. The evaporation temperature was measured by a W/Re-5/20 thermocouple. The electron wavelength was determined from the diffraction patterns of ZnO recorded before and after the GED experiments on [ZnTTDPz]. The total intensity curves were obtained from two nozzle-to-plate distances,  $L_1=598$  mm and  $L_2=338$  mm.

Firstly, we have studied mass spectra of [ZnTTDPz] in the range from 1 to 2500  $m/e$  using ionizing electron energy 50 eV at various temperatures. The typical mass spectrum recorded at 588 °C is shown in Figure 1 and the relative abundance of ions is presented in Table 1. It was found that [ZnTTDPz] has a high sublimating temperature and the molecular ion appears in the mass spectra recorded above

$\sim 500$  °C. Sublimation of [ZnTTDPz] under reduced pressure (about  $10^{-3}$  bar) with continuous N<sub>2</sub> gas flow was also observed at 450–550 °C.<sup>[6]</sup> The high sublimating temperature in our more strict vacuum conditions (about  $10^{-7}$  bar) is surely determined by strong intermolecular interactions present in the solid (crystalline) state of [ZnTTDPz] (especially formation of coordination polymer chains<sup>[6]</sup>).

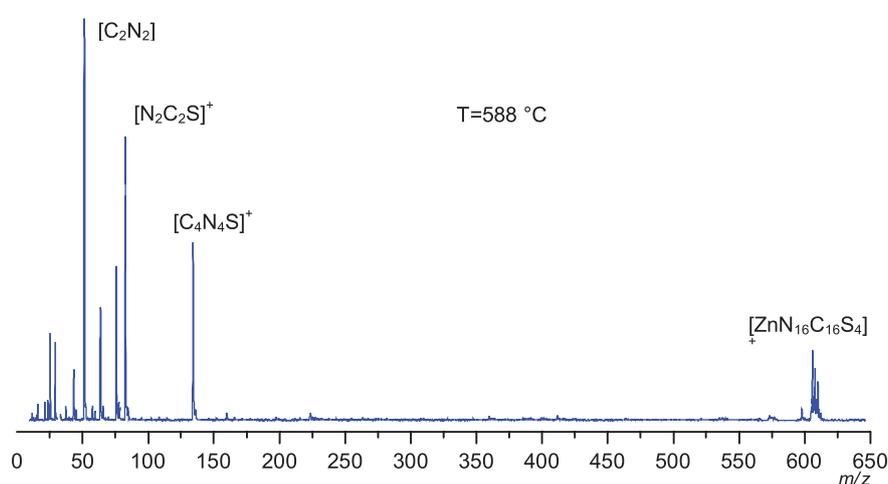
**Table 1.** Relative abundance of ions from [ZnTTDPz] at conditions of GED experiment.

Ion <sup>a</sup>	$m/e$	$I_{av}^{b, \%}$
[ZnN <sub>16</sub> C <sub>16</sub> S <sub>4</sub> ] <sup>+</sup>	609	12
[C <sub>4</sub> N <sub>4</sub> S] <sup>+</sup>	136	26
[N <sub>2</sub> C <sub>2</sub> S] <sup>+</sup>	84	75
[N <sub>2</sub> C <sub>4</sub> ] <sup>+</sup>	76	32
[C <sub>3</sub> N <sub>2</sub> ] <sup>+</sup>	64	87
[C <sub>2</sub> N <sub>2</sub> ] <sup>+</sup>	52	100

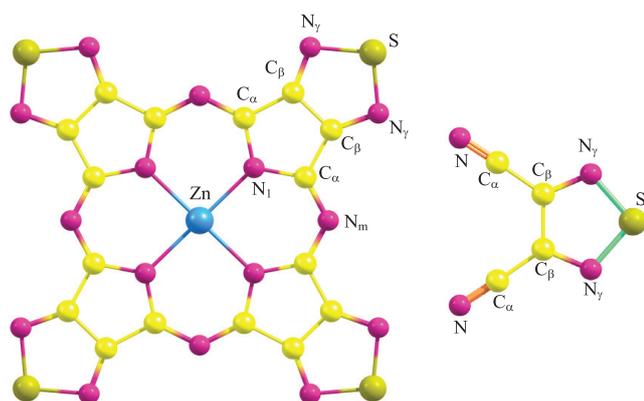
<sup>a</sup>approximate assignment

<sup>b</sup>most abundant isotope

It is known that metal complexes of tetrapyrrolic macrocycles, such as phthalocyanines and porphyrins, have high thermal stability. In the absence of substituents they do not undergo decomposition during sublimation and the molecular ion is the prevailing ion in the mass spectra of their vapours. Thus, the mass spectrum of zinc phthalocyanine, [ZnPc], contains such ions as: the parent ion [ZnPc]<sup>+</sup> (most intensive, 100 %), the intensive doubly charged parent ion [ZnPc]<sup>2+</sup> (33 %), as well as minor fragmentation ions [Zn+ $\frac{1}{2}$ Pc]<sup>2+</sup> (11 %), [Zn+ $\frac{1}{4}$ Pc]<sup>+</sup> (6 %) and [ $\frac{1}{4}$ Pc]<sup>+</sup> (4 %).<sup>[11]</sup> In contrast, analyzing the mass spectra of [ZnTTDPz] recorded during GED/MS experiment we came to the conclusion that its sublimation, unlike [ZnPc], is accompanied by partial decomposition. The heaviest observed ion [ZnN<sub>16</sub>C<sub>16</sub>S<sub>4</sub>]<sup>+</sup> at  $m/z=609$  a.m.u. corresponding to the parent ion [ZnTTDPz]<sup>+</sup> disappears at higher temperature or prolonged exposition. This parent ion has lower intensity than another heavy ion [C<sub>4</sub>N<sub>4</sub>S]<sup>+</sup> at  $m/z=136$  a.m.u. which remains in the mass spectra after disappearance of the parent ion [ZnN<sub>16</sub>C<sub>16</sub>S<sub>4</sub>]<sup>+</sup>. The [C<sub>4</sub>N<sub>4</sub>S]<sup>+</sup> ion corresponds to  $\frac{1}{4}$ (TTDPz) and can be



**Figure 1.** Typical mass spectrum (EI, 50 eV) recorded at 588 °C.



**Figure 2.** Molecular structures of [ZnTTDPz] and  $C_4N_4S$  with atom numbering.

assigned to the  $C_4N_4S$  molecular species – 1,2,5-thiadiazole-3,4-dicarbonitrile which presents in the vapor together with [ZnTTDPz] at the GED experiment temperature.

The electron diffraction patterns were recorded simultaneously with the mass spectrum at 587(5) °C. Final least-square analysis of the electron scattering molecular intensity was performed with the assumption that the vapour over the sample of solid zinc(II) tetrakis(1,2,5-thiadiazolo)porphyrizine consists of [ZnTTDPz] molecules and the dinitrile  $C_4N_4S$  as its decomposition product. The best fitting was obtained for the vapour composition

[ZnTTDPz]/ $N_4C_4S=0.1/0.9$  in overall agreement with the ion intensity ratio in the mass spectrum at the same conditions.

Additionally the molecular structures of [ZnTTDPz] and  $C_4N_4S$  were optimized under  $D_{4h}$  and  $C_{2v}$  symmetry restrains, respectively, at the B3LYP/cc-pVTZ theory level using Gaussian 03 program.<sup>[12]</sup> The selected structural parameters obtained by gas electron diffraction and DFT calculations are given in the Table 2. It can be seen that the values of structural parameters produced by the analysis of GED data for both compounds existing in gas phase – the macrocyclic complex [ZnTTDPz] and the dinitrile  $C_4N_4S$  – are in satisfactory agreement with the available single crystal X-ray diffraction data.<sup>[6,13]</sup>

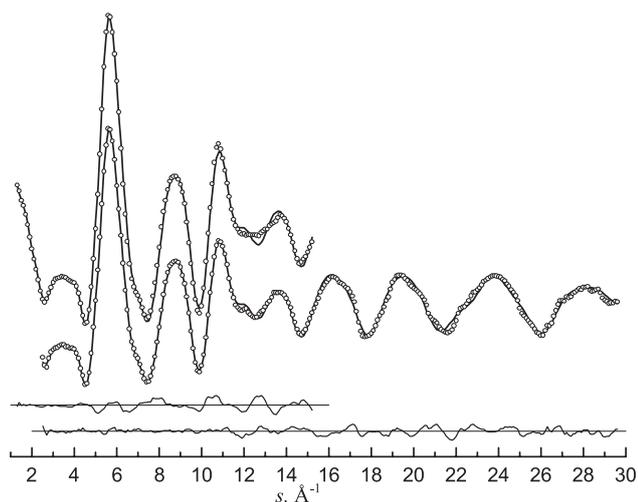
The results of GED refinement and DFT calculations show that the [ZnTTDPz] molecule has a planar structure of  $D_{4h}$  symmetry in the gas phase. This indicates that the displacement of the Zn atom out of plane of the molecule found in the crystal structure of [ZnTTDPz] is caused by intermolecular interactions or more exactly by «the ( $M \cdots N_\gamma$ ) coordination bonding» as it previously was reported by Awaga *et al.*<sup>[6]</sup> The Zn-N coordination bond with central nitrogens in gaseous [ZnTTDPz] is shorter by  $\sim 0.02$  Å than in crystalline [ZnTTDPz] due to planar structure of the macrocyclic ligand. At the same time it is longer by  $\sim 0.04$  Å than in the gas-phase [ZnPc].<sup>[13]</sup> The Zn-N difference between [ZnTTDPz] and [ZnPc] reflects the effect of expansion of the macrocyclic core observed when external benzene rings in the phthalocyanines are replaced by heterocyclic 1,2,5-thiadiazole moieties in TTDPz macrocycle. It should be noted that the expansion of the macrocyclic core is accompanied by rearrangement of all

**Table 2.** Structural parameters of [ZnTTDPz] and  $C_4N_4S$  according to GED, X-ray and B3LYP/cc-pVTZ calculations.\*

[ZnTTDPz]				$N_4C_4S$			
Parameter	GED $r_{hi}$	DFT $r_c$	X-ray <sup>[6]</sup> $r$	Parameter	GED $r_{hi}$	DFT $r_c$	X-ray <sup>[13]</sup> $r$
Bond distances				Bond distances			
Zn–N <sub>1</sub> <sup>b</sup>	2.023(12)	2.024	2.043(5)	S–N <sub>γ</sub>	1.641(4)	1.636	1.623(5)
N <sub>1</sub> –C <sub>α</sub> <sup>**</sup>	1.382(4)	1.375	1.380(7)	N <sub>γ</sub> –C <sub>β</sub>	1.326(4)	1.320	1.329(6)
C <sub>α</sub> –N <sub>m</sub>	1.324(4)	1.318	1.326(7)	C <sub>β</sub> –C <sub>α</sub>	1.414(6)	1.425	1.442(5)
C <sub>α</sub> –C <sub>β</sub> <sup>**</sup>	1.448(6)	1.458	1.456(8)	C <sub>α</sub> –N <sub>m</sub> <sup>**</sup>	1.159(5)	1.151	1.140(8)
C <sub>β</sub> –N <sub>γ</sub>	1.322(4)	1.315	1.327(7)				
N <sub>γ</sub> –S <sup>**</sup>	1.658(4)	1.654	1.641(5)				
C <sub>β</sub> –C <sub>β</sub>	1.411(6)	1.422	1.408(8)				
Bond angles				Bond angles			
ZnN <sub>1</sub> C <sub>α</sub> <sup>**</sup>	124.2(9)	124.2	124.0(5)	N <sub>γ</sub> SN <sub>γ</sub>	98.2(10)	98.8	99.6(3)
C <sub>α</sub> C <sub>β</sub> C <sub>β</sub>	107.7(10)	107.0	107.2(5)	N <sub>γ</sub> C <sub>β</sub> C <sub>β</sub>	112.7(5)	113.4	113.5(3)
N <sub>1</sub> C <sub>α</sub> C <sub>β</sub> <sup>**</sup>	106.5(5)	107.1	107.5(5)	SN <sub>γ</sub> C <sub>β</sub>	108.2(7)	107.2	106.7(3)
C <sub>β</sub> C <sub>β</sub> N <sub>γ</sub> <sup>**</sup>	116.1(7)	115.1	114.9(5)	N <sub>γ</sub> C <sub>β</sub> C <sub>α</sub>	122.4(6)	121.4	120.7(5)
C <sub>α</sub> N <sub>1</sub> C <sub>α</sub>	111.6(6)	111.7	110.6(5)	C <sub>β</sub> C <sub>α</sub> N <sub>m</sub>	180.0 fix	180.0	178.6(6)
C <sub>α</sub> N <sub>m</sub> C <sub>α</sub>	124.5(7)	125.7	124.2(5)				
N <sub>γ</sub> SN <sub>γ</sub>	101.8(10)	100.1	100.7(3)				

\*bond distances in Å, bond angles in deg.

\*\*parameters refined independently; other parameters were constrained to independent parameters



**Figure 3.** Functions of the molecular scattering intensity  $sM(s)$ : experimental (dots), and theoretical (line), and the difference function  $\Delta sM(s)$  for the vapor containing species  $[ZnTTDPz]$  and  $N_4C_4S$  with mole fraction ratio 0.1:0.9.

geometrical parameters of the molecule. In contrast with the above-mentioned  $[ZnTTDPz]$  molecule the GED geometry of the dinitrile molecule  $C_4N_4S$  in gas phase is similar to the X-Ray geometry in a crystalline state.<sup>[13]</sup>

Investigation of gas-phase behavior of other porphyrazine analogues with fused 1,2,5-thiadiazole rings is in progress.

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