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To the limit of gas-phase electron diffraction: Molecular structure of magnesium octa(m-trifluoromethylphenyl)porphyrazine

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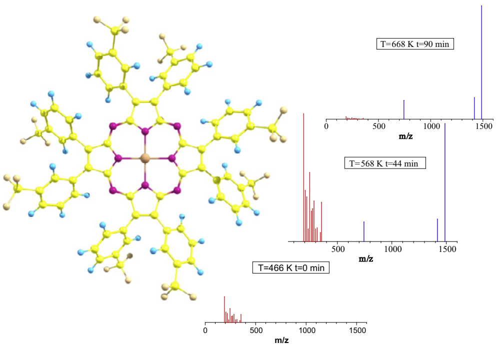
HIGHLIGHTS

- Molecular structure of $MgC_{72}H_{32}N_8F_{24}$ was studied by combined GED/MS experiment.
- Electronic structure of $MgC_{16}H_8N_8$, $MgC_{64}H_{40}N_8$ and $MgC_{72}H_{32}N_8F_{24}$ was studied by DFT.
- π-Systems phenyl rings and macrocycle conjugation defines the conformations.
- Nyquist–Shannon–Kotelnikov theorem is discussed concerning study of large molecules.
- The HOMO–LUMO gap regulation by the substituent is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The gas-phase molecular structure of the magnesium octa(m-trifluoromethylphenyl)porphyrazine ($MgC_{72}H_{32}N_8F_{24}$) has been studied by a synchronous gas-phase electron diffraction and mass spectrometric experiment at $T = 667(10)$ K in combination with DFT calculations using B3LYP hybrid method and triple-ζ valence basis sets. The molecule has an equilibrium structure of D_4 symmetry. The following values of selected internuclear distances have been determined: r_{h1}, Å: r(Mg–N) = 1.979(5), r(N–C) = 1.363(3), $r(N_{mezo}–C) = 1.334(4)$, $r(C_{pyr}–C_{Ph}) = 1.469(3)$, $r(C_{Ph}–CF_3) = 1.510(5)$, r(C–F) = 1.349(3), $r(C_\alpha–C_\beta) = 1.466(3)$, $r(C_\beta–C_\beta) = 1.380(7)$. A slight (less than 1 to 2 degrees) twisting deformation of the macrocycle from planarity, caused by the presence of the eight bulky $PhCF_3$ substituents, planes of which are turned by 132.6(9) degrees relative to the adjacent pyrrole rings, has been found. The deviation of phenyl ring planes from 90 degrees orientation is caused by stabilizing donor–acceptor interactions between π-natural orbitals of pyrrole and phenyl moieties. Substitution effects and coordination bonding in magnesium porphyrazine complexes, MgPz, $MgPzPh_8$ and $MgPz(CF_3Ph)_8$, are discussed. Sensitivity of GED data to long range interatomic distances of large molecules has been shown.

Introduction

The first successful preparation of octaphenylporphyrazines was reported in 1937 by Cook and Linstead [1]. The parent compound – the unsubstituted porphyrazine (or tetraazaporphyrin) and its metallic derivatives, including the Mg(II) complex (MgPz), were synthesized in 1952 [2]. Despite their long history, the information about porphyrazines and especially about their structural properties, compared to a plethora of studies of porphyrins and phthalocyanines, is relatively scant.

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X-ray studies of the structures of two octasubstituted magnesium porphyrazines, aqua-(2,3,7,8,12,13,17,18-octakis(methylthio)-porphyrazine-N,N′,N″,N‴)-magnesium [3] and aqua-(1,2:3,4:5,6:7,8-tetrakis((b)1,4-dithia-18-crown-6)porphyrazine-N,N′,N″,N‴)-magnesium hydrate [4,5] were reported. The macrocycles in these studies are slightly concave, but this is probably due to the water molecule attached axially to the magnesium atom, displacing it out of the plane of four central nitrogen atoms. The Mg–N distances are 2.025–2.046 Å [3], 2.007–2.054 Å [4] and 2.011–2.057 Å [5]. There is also a study of spectroscopy of single Mg tetraazaporphyrin molecules isolated in solid xenon [6].

Optimized geometries, electronic structures and NMR spectra of porphyrazine metal complexes (including MgPz) were recently studied by density functional theory calculations (B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels) [7,8]. Molecular structure, electronic structure and vibrational spectra of magnesium tetrakis(thiadiazole)porphyrazine was also studied theoretically (DFT calculations, B3LYP/6-31G(d) level) in 2005 [9]. Molecular and electronic structure and IR and Raman spectra of magnesium tetra-2,3-pyrazino-porphyrazine were studied by DFT calculations (B3LYP/6-31G(d) level) [10]. In all cases, the molecules were found to have D_{4h} symmetry with planar macrocycle.

Magnetic circular dichroism of tetraazaporphyrin metal complexes (including MgPz) was investigated in a computational study based on time-dependent density functional theory [11]. Geometry optimization, singlet–triplet energy gap, and electronic absorption spectra DFT calculations for MgPz were performed in study [12] at the PBE0/TZVP level of theory. Again, the molecule was found to possess D_{4h} symmetry with Mg–N bond length of 1.974 Å. It should be noted that this value is significantly smaller than the bond lengths found in X-ray studies [3–5].

The present work, to our best knowledge, is the first gas-phase structural study of a porphyrazine. The combination of a synchronous gas-phase electron diffraction and mass-spectrometry (GED/MS) experiment with DFT computations using triple-ζ valence basis sets has proved itself to be an good technique for studying large macroheterocyclic molecules [13–18]. In addition, presently there are very few GED studies of molecules consisting of more than 100 atoms and we hope that this investigation of a 137-atom molecule will be a new milestone in studies of structures of large molecules in the gas phase.

Computational

Theoretical studies of the unsubstituted magnesium porphyrazine ($MgC_{16}H_8N_8$, **I**), magnesium octaphenylporphyrazine ($MgC_{64}H_{40}N_8$, **II**) and octa(m-trifluoromethylphenyl)porphyrazine ($MgC_{72}H_{32}N_8F_{24}$, **III**) have been carried out using density functional theory (DFT) calculations utilizing the B3LYP (Becke + Slater + HF exchange and LYP + VWN correlation) hybrid functional. Preliminary calculations of **III**, intended for obtaining starting geometries and Hessian matrices for further higher level computations, were carried out using the 6-31G** basis sets [19,20]. In the higher level computations (geometry optimizations, force field and NBO calculations), C, H, N and F atoms were described by Dunning triple-ζ valence basis sets [21] with polarization functions (C: $d = 0.72$, H: $p = 1.0$; N: $d = 0.98$; F: $d = 1.62$) and a diffuse function in case of F ($p = 0.074$). Mg atom was described by McLean and Chandler triple-ζ valence basis set [22] with polarization function ($d = 0.234$). These computations will be referred to as B3LYP/TZV. All calculations mentioned above were performed

Table 1
Conditions of the synchronous GED/MS experiments.

	1	**2**	**3**
Nozzle-to-plate distance, mm	598	338	338
Number of recorded films	3	2	2
Primary electron beam current, μA	1.4	1.8	1.9
Accelerating voltage[a], kV	92	92	93
Temperature of effusion cell, K	663(4)	668(6)	667(3)
Wavelength of electrons[b], Å	0.038668(5)	0.038730(5)	0.038529(5)
Exposure time, s	130	190	150
Residual gas pressure in the diffraction chamber, Torr	$2 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-6}$
Scattering angles, Å^{-1}	1.3–16.3/ 0.1	2.5–32.0/ 0.1	2.5–30.8/ 0.1
Ionization voltage, V	50(1)	50(1)	50(1)

[a] Approximate value.

[b] Accurate wavelengths of electrons were calibrated using diffractions pattern of polycrystalline ZnO.

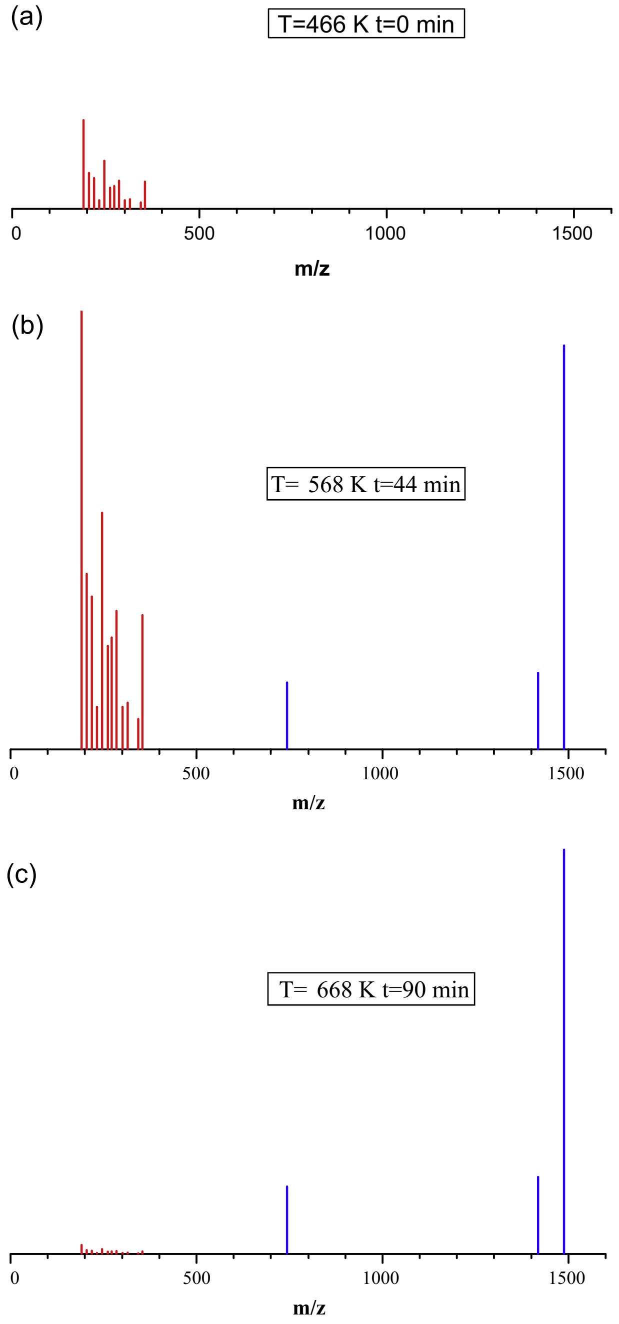

Fig. 1. Mass spectra were recorded at different times after the start of heating of sample.