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GraphicalAbstract

The synthesis, characterization and computional investigation of new metalloporphyrazine containing 15-membered S_4 donor macrocyclic moleties

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The synthesis, characterizationand computional investigation of newmetalloporphyrazine containing 15-membered S₄ donor macrocyclic moieties

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ABSTRACT:

In this study, an improved synthesis of 1,5-bis(2-formylphenyl)-1,5-dithiapentane(3) has been performed according to the literature in a high yield. 1,5-Bis (2-benzyl alcohol)-1,5-dithia pentane (4) was prepared by the reduction reaction of precursor compound in high yield via solvent-free conditions. Treatment of substituted benzylic alcohol with bromotrimethylsilane in dry acetonitrile in the presence of NaI resulted the formation of desired iodine derivative (5) in very high yield. 7,8-dihydro-6H, 14H, 19H-dibenzo[bj][1,12,5,8]tetradithiacyclopentadecine-16,17-dicarbonitrile (7) was synthesized by the reaction of compound 7 and dithiomaleonitrile disodium salt. Magnesium porphyrazine carrying symmetrically four 15-membered tetrathia macrocycles has been synthesized by the cyclotetramerization reaction of dicarbodinitrile compound (7) in the presence of magnesium butoxide according to the Linstead procedure. We focused on the prediction of the geometry optimization, normal mode frequencies, UV absorption spectra, chemical shifts and electronic properties of the compound by using B3LYP method with 6-31G(d) basis set. These novel compounds were characterized by a combination of elemental analysis, ¹H, ¹³C NMR, FT-IR, UVvis and MS spectral data. An X-ray crystal structure of dicarbodinitrile compound (7) is also presented. The computed results are very close to the obtained experimental results by spectroscopic techniques.

Keywords: Tetrathia macrocyle; Metalloporphyrazines; Macrocyclization; Green chemistry; Template effect; Computional chemistry.

1. Introduction

One of the important cornerstones in tetrapyrrolic macrocyclic systems is the porphyrazines.¹ Porphyrazines are similar to phthalocyanines so they can also be used in similar applications as phthalocyanines. In contrast, porphyrazines and their

derivatives such as aminoporphyrazines, porphyrazinols and porphyrazine-thiolates have been less studied since their first sythesis, which took place almost 60 years ego.²⁻⁴ Porphyrazines have found applications in diverse areas such as industrial dyes and pigments, electrocatalysts, electrochromic displays, PDT, chemical sensors, Langmuir-Blodgett films, liquid crystals and non-linear optics, including their application in material science.⁵⁻⁷ The first synthesis of crown-fused porphyrazines has been accomplished by groups of Hoffman and Nolte.⁸⁻¹⁰ Porphyrazine derivatives, which contain soft sulfur donor atoms, play an important role in affecting the solid-state interactions and the sulfur atoms in the macrocyclic unit also give the opportunity to bind soft transition metal cations.¹¹⁻¹³ In addition to that, the electron-withdrawing effect of the maleonitrile moiety may reduce the electron-donating ability of the sulfur donors in macrocyclic unit and this kind of heteroatom strongly perturbs the porphyrazine grand state transition shifting to the visible-to-near-IR region.¹⁴

For several decades, since their discovery and the pioneering study by Pedersen,¹⁵ innumerable studies on crown ethers and their anologues with different donor atoms such as oxygen, nitrogen, sulfur have been carried out and their complexation ability has been extensively studied.¹⁶ Thioether crowns are known to coordinate "soft" metal cations such as low-valent transition metals and group IB and IIB in either an exo or endocyclic mode.¹⁷ Thia-macrocyclic metal complexes are highly stable and have received great attention to their biological activities including different applications such as antitumor, antibacterial, antiviral and anticarcinogenic properties.¹⁸ Porphyrazine-linked thia macrocycles are interesting compound due to selective extractant properties for soft metal cations and model capability for the active sites of some enzymes.¹⁹

In recent years, Density Functional Theory (DFT) methods have widely been used for the interpretation and prediction of complex systems behavior at an atomic scale, the developments in the methodological, and software have transformed ab initio and DFT approach in a completeyl interdisciplinary science from molecular sciences to the diverse fields of chemistry.²⁰ It is known that the DFT (B3LYP) method adequately takes electron correlation contributions into account, which are especially important in systems containing extensive electron conjugation and electron lone pairs. Nowadays, it is commonly agreed that electronic structure calculations of excited states of coordination compoundare very important complement to spectroscopic techniques. Nevertheless, due to the size, the state degeneracies, the dynamical correlation and relativistic effects, theoretical calculation of ground and excited state properties of metal complexes which use computational methods confront some difficulties. In addition to that, DFT methods are also extensively used in order to simulate the electronic spectra of metal complexes despite the fact that the most appropriate method to describe the ground state and excited state properties of these kind of compounds seem to be the multiconfigurational self-consistent-field one including relativistic effects. The most popular among them is the time-dependent DFT (TD-DFT) approach.²¹

In the present study, we synthesized and characterized a novel metalloporphyrazine having four tetrathia crown ether moieties. X-Ray crystal structural analyses concerning the dicyano compound has also been performed. In addition to detailed synthesis procedures, we also theoretically investigated the geometry optimization of precursor dicyano compound (7) and magnesium porphyrazine by means of B3LYP method with 6-31G(d) basis set.

2. Results and Discussion

2.1. Synthesis

1,5-Bis(2-formylphenyl)-1,5-dithiapentane (3) can be prepared in high yield using a step known synthetic routeas outlined in Scheme 1. There are many reports for the synthesis of compound **3**. One of them, the dicarboxylic acid derivative of the skeletal framework was then reduced to the alcohol and oxidised over manganese dioxide to form dialdehyde (3). This compound has been synthesized previously in low yields, different ways and with different physical properties.²² Beloglazkina,^{22b} Naeimi^{22c} and co-workers synthesized compound 3 under similar reaction conditions. However the compound (3) we obtained is purer than those mentioned in the literature in terms of spectral data. 2-Nitrobenzaldehyde, propane-1,3-dithiol and inorganic base should be sufficient to achieve quantitative conversion of desired compound in 89% yield. The present S_NAr-reaction is high-yielding compared with similar reactions. According to the above mentioned literature,^{22a,22b,22c} the melting point of this compound was 56-57, 52-53 and 112-114 °C, respectively. These data are very different from our result. The structure of the compound produced by us was confirmed by spectroscopic data. Compound 3 displayed the expected molecular ion peak at $m/z = 317 [M+1]^+$. In the ¹H and ¹³C NMR spectra of this compound, the characteristic resonances of the aromaticaliphatic protons and carbons were similar to those of the literature mentioned above but our spectra for compound 3 are the clearest of all.

The preparation of 1,5-bis(2-benzyl alcohol)-1,5-dithiapentane (**4**) was first carried out by Lindoy,^{22a} Castro^{23a,b} and then Taylor et al.^{22e} In these mentioned literature the dicarboxylic acid derivative of thia ether bridge compounds were reduced to the alcohol using a variety of reducing agents such as LiAlH₄ and NaBH₄. Using ecologically safe reagents or media in organic reaction is an important paradigm in today's chemistry. Reduction reactions, carried out in green chemistry media, have received great attention with advantages such as simple work-up procedure energy saving, avoidance of solvent waste and toxicity.²⁴ We reducted the precursor compound with an equivalent amount of NaBH₄ in the presence of wet SiO₂ under solvent free conditions with 85% conversion within 10 min. FT-IR, ¹H and ¹³C NMR spectroscopic data concerning structural characteristics were in accord with proposed structure and literature mentioned above. The structure of this compound was also confirmed by its MS spectrum, in which the peak at m/z = 320 corresponding to [M]⁺ was observed.



Scheme 1. The synthesis of MgPz

The conversion of alcohols into iodine derivatives is a very important transformation process in organic chemistry. For this reason, convenient routes have been literature.²⁵ Examples reported in the have been reported utilizing KI/BF₃.Et₂O,^{25b}Ph₃P/I₂^{25c,e} or trimethylsilyl chloride.^{25a,f} A comparison of the known methods showed the bromotrimethylsilane/NaI to be more convenient due to iodotrimethlysilane generated in situ. This reaction was found to proceed smoothly at room temperature in 20 min. Benzylic OH groups could easily be substituted by iodide groups in high yield (92%) using this procedure. Treatment of substituted benzylic alcohol (4) with the three equivalent of bromotrimethylsilane in dry acetonitrile in the presence of an equivalent amount of NaI resulted in the formation of desired iodide derivative (5). The ¹H NMR spectrum of 5 clearly showed the characteristic emerged signals at $\delta = 4.61$ ppm concerning iodide substitution. The other proton-NMR resonances of 5 closely resembled those of the precursor compound (4). The protondecoupled ¹³C NMR spectrum of 5 also clearly indicated the presence of expected signals. The disappearance of the characteristic signals concerning benzylic OH, along with the appearance of the chemical shifts at $\delta = 4.66$ ppm corresponding to CH₂-I carbon indicate the conversion reaction.²⁶ A diagnostic feature of iodination formation from compound 4 is the disappearance of the O-H resonances at 3308 cm^{-1} in the IR spectrum. The mass spectrum of this compound shows the molecular ion peak as m/z: 541.956 $[M+1]^+$ and the other bigger fragment ions are observed together with the corresponding leaving groups (Fig.1).



Figure 1. The mass spectrum of 5

The substituted tetrathia crown compound can be synthesized using a four step synthetic route as outlined in Scheme 1. Treatment of the compound 5 with cis-1,2dicyano-1,2-ethylenedithiolate disodium salt (6) in dry acetonitrile resulted in the formation of desired 15-membered macrocycle 7 in 19% yield (Scheme 1). A method for the synthesis of thia crown ethers developed by Buter and Kellogg²⁷ involves Cs_2CO_3 mediated cyclization of dithiole and a dihalide in DMF by high-dilution technique. Using this method, tetrathia crowned macrocycles have been synthesized in low yield (10%). This situation could be attributed an "inside-out" conformation in which the electron densities of the sulfur atoms point out the ring.²⁸ In addition to that, aromatic-aliphatic chains crown thio ethers with rigid aromatic moieties adopt only a limited number of possible ring conformations and the effective ring size is reduced.²⁹ The macrocycle (7)was then prepared by straightforward condensation reaction in dry acetonitrile media in 19% over all yield as shown in Scheme 1. The structure of macrocycle (7) was proven by a combination of NMR, IR, elemental analysis, MS and X-ray spectral data. The ¹H NMR spectrum of this macrocycle is very similar to the precursor compound (5) except for the formation of novel CH₂-S chemical shifts at $\delta = 4.27$ ppm as expected. Protondecoupled ¹³C NMR spectrum of 7 was in good agreement with proposed structure. The characteristic signals concerning SCH₂, CH₂, Ar-CH₂, C=C and C=N groups at δ =34.58, 30.09. 38.31, 127.53 and 112.80 ppm, respectively, clearly suggested that macrocyclization has occurred (Fig.2). In the IR spectrum of this compound, the appearance of intense C=N vibrations at 2208 cm⁻¹ also supported the formation of macrocycle. The ESI mass spectrum of this compound exhibited a molecular ion peakat m/z = 426.57, which corresponds to $[M]^+$, and also supports the structure.



Figure 2. The structure of 7

The cyclomerization of 15-membered tetrathia macrocycle substituted cis-1,2-dicyano-1,2-ethylene dithiolate based on a template effect of magnesium butoxide has been used to generate the microcrystalline magnesium porphyrazine [MgPz] in 23%. An attempt to obtain good-quality single crystals of MgPz was unsuccessful. In addition to that, the low solubility of this compound does not permit to obtain good-quality NMR spectra. The ¹H NMR spectrum of this compound, the characteristic signals relating to the CH₂S, CH₂, Ar-CH₂S and aromatic group linked with tetrathia crowned macrocycle units gave significant resonances of the proposed structure at $\delta = 3.21, 1.97, 5.40$ and the range of 7.40-6.76 ppm, respectively. The peak related to the C=N group in the 13 C NMR spectrum of MgPz vanished in the case of metalloporphyrazine. In addition to that, the appearance of C=N signals at $\delta = 140.05$ ppm for MgPz concerning the inner core instead of C=N resonances in 7 supported the formation of desired compound. According to the IR spectrum of MgPz, the stretching vibrations for the C=N groups at 2208 cm⁻¹ for precursor compound disappeared and a novel resonance appeared at 1626 cm⁻¹ that is attributed to the C=N groups in the porphyrazine core. The ESI mass spectrum of MgPz was measured as $m/z = 1728.16 [M]^+$ and is in good accord with the proposed structure.

The correlation analysis between the experimental and theoretical results computed in this work has been done to observe experimental consistency with the chemical shifts calculated by using B3LYP/6-31G(d) level. In order to check the performance of the theoretical approach, correlation analysis has been done for full set of the chemical shifts for compound **7** considered in gas phase and chloroform (Table 1). The correlation par-ameters of **Com.7** were calculated as $R^2 = 0.9935$ in gas phase and $R^2 = 0.9937$ in solvent (Fig. 3). Theoretical ¹H and ¹³C chemical shift values calculated with GIAO-DFT

with respect to TMS of **Com.7** are significantly in agreement with the experimental values.

Atoms	Exp	Gas phase	phase Chloroform	
C7	134.39	137.17	137.08	
C3	127.53	134.45	134.59	
C8	136.99	129.91	129.35	
C10	123.19	125.06	125.69	
C6	128.83	125.15	125.15	
C5	132.69	123.27	123.73	
C4	130.29	121.16	121.67	
C11	112.80	102.74	103.59	
C9	38.31	44.17	44.47	
C2	34.58	38.88	38.96	
C1	30.09	29.98	29.79	
H3	7.07	7.47	7.51	
H6	7.34	7.43	7.41	
H5	7.21	7.03	7.15	
H4	7.15	6.97	7.11	
H9	4.27	4.27	4.35	
H2	2.97	2.74	2.82	
H1	1.95	1.25	1.26	

Table 1. Values of the ¹H and ¹³C NMR chemical shifts of **Com.7** as computed by using B3LYP method with 6-31G(d) basis set and available experimental data





2.2. Electronic properties

Figure 4 shows the absorption spectrum of symmetrically 15-membered S_4 macrocycles tetra substituted porphyrazinato magnesium complex. Metal porphyrazines show an intense Soret (B) band at around λ_{max} <400 nm and a significant sharp bands that have their principal absorptions at around λ_{max} >600 nm.³⁰ The absorption spectrum of MgPz taken in chloroform at room temperature exhibits a strong absorption at $\lambda_{max} = 685$ nm which is because of the $\pi \to \pi^*$ transition and is referred to as a Q band which relates to a strong low-energy absorbance. The other absorption is accompanied by a slightly higher energy shoulder at $\lambda = 625$ nm. The sharp single band at $\lambda_{max} = 685$ nm is characteristic of tetrapyrrolic systems such as porphyrazine, phthalocyanine and derivatives with D_{4h} symmetry.^{8,31} However, another intense absorption at around $\lambda = 383$ nm can be attributed to the so-called N-band, which is strengthened with respect to the Soret band. The Q and Soret band absorptions should be related to $\pi \rightarrow \pi^*$ transition from a_{2u} HOMO to the double degenerate e_g LUMO orbitals.³² The very broad absorption at around $\lambda_{max} = 519$ nm is assigned to an $n \rightarrow \pi^*$ transition of the non bonding electrons of the peripheral sulfur and nitrogen atoms, which are associated with porphyrazine core π system. This strong coupling of the nonbonding electrons with the π -system also resulted in considerable broadening because of vibrational fine structure.³³



Figure 4. The UV-vis spectrum of MgPz ($1x10^{-5}$ M in chloroform)

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies are important parameters in molecular orbital theory. The energy gap between the HOMO-LUMO orbitals characterizes the electron conductivity and the spectroscopic properties of the molecules.

The electronic gap values are calculated as 3.8374 eV for **Com.7** and 2.1560 eV for **MgPz** at B3LYP/6-31G(d) level as seen in Table 2. The optic gap values are calculated as 3.7547 eV for **Com.7** and 1.8644 eV for **MgPz**. These energy gap values show that charge transfer in the molecule exists. The high electron density is mostly localized on the N atom as can be seen in Figure 5a,b. Typically, organic semiconductors with a bandgap of about 3 eV are applied as photoactive materials, but the observed open-circuit voltages are only in the range of 0.5-1 V.³⁴ The inorganic semiconductor materials used to make photovoltaic cells have energy band gaps within the range 1.1-1.7 eV, that is they are near to the optimum energy band gap (1.5 eV) for photovoltaic solar energy conversion by a single junction solar cell.³⁵ Accordingly, the molecule is a candidate for inorganic semiconductor materials. In addition, the calculated self-consistent field (SCF) energies of **Com.7** and **MgPz** are calculated as -2513.178 a.u. and -10253.588 a.u., respectively.

Electronic parameters	Com. 7	MgPz
HOMO (eV)	-6.3876	-5.8589
LUMO (eV)	-2.5503	-3.7029
ΔE=LUMO-HOMO (eV)	3.8374	2.1560
TD/LUMO-HOMO (eV)	3.7547	1.8644
I (eV)	6.3876	5.8589
A (eV)	2.5503	3.7029
χ (eV)	4.4689	4.7809
Hardness (ŋ)	1.9187	1.0780
Softness (S)	0.5212	0.9277

 Table 2. Electronic parameters of the compounds.

The electrostatic Surface Potential (ESP) that is associated with partial charge and electronegativity plots exhibit the distribution of charge of compounds with respect to the difference between positive and negative charge.³⁶ The ESP map of the surface presented in molecular size shows the shape and electrostatic potential value. Colours seen on the ESP surfaces indicate different values of the electrostatic potentials. Red colour represents the regions carrying the most electronegative potentials, i.e. electron rich regions, blue colour represents regions of most positive potentials, i.e. electron poor regions and green colour means zero potential. Mentioned potentials increase in the following order: red<orange<yellow<green
blue. The deepest blue region defines strongest attraction and the deepest red describes strongest repulsion. However, the electrophilic reactivity has been presented by negative (red) regions but nucleophilic reactivity has been shown by the positive (blue) regions. The ESP of **Com.7** and **MgPz**

changes from -0.04368 a.u. to 0.04368 a.u. for **Com.7** and from -0.007525 a.u. to 0.007525 a.u. for **MgPz**, respectively, as seen in Figure 5a,b. The energy gap $[(\Delta E = LUMO-HOMO)calcd.] = 2.1560 \text{ eV}]$ of **MgPz** is significantly smaller than **Com.7** which can be attributed the introduction of electron donating sulfur atoms at the α positions of porphyrazine. Especially sulfur moieties at the α positions in porphyrazine can destabilize the HOMO energy,³⁷ so that the HOMO-LUMO value becomes smaller than **Com.7**. As shown in Figure 6 for **Com.7**, LUMO electrons are mostly localized on double and triple bonded groups such as C=C and C=N. On the other hand, HOMO electrons are mostly localized on the aromatic and thia ether groups. The LUMO electrons are mostly localized on carbon and sulfur atoms which are linked pyrrole units.

Also the chemical hardness (η) and electron affinity (A) of the molecules can be calculated from the HOMO-LUMO orbitals. The chemical hardness values of **Com.7** and the **MgPz** are 1.9187eV and 1.0780 eV, respectively. The electron affinity (A), electronegativity (χ), chemical hardness (η) and softness (σ) of the molecules are given in Table 2. Hardness (η) data of **Com.7** and **MgPz** are calculated as 1.9187 and 1.0780, re-



Figure 5a. The molecular electrostatic potential surface map calculated at B3LYP/6-31G(d) level of **Com.7**.

spectively. The hardness character of **MgPz** decreases according to the precursor compound and on the contrary, the softness character increases because of the decrease of absolute electronegativity of porphyrazine core.³⁸



Figure 5b. The molecular electrostatic potential surface map calculated at B3LYP/6-31G(d) level of **MgPz**.



Figure 6. The HOMO and LUMO energies for **Com.7** with B3LYP/6-31G(d) basis set in gas phase.



Figure 7. The HOMO and LUMO energies for **MgPz** with B3LYP/6-31G(d) basis set in gas phase

2.3. X-ray structure

The X-ray structural determination of the title compound confirms the assignments of its structure from spectroscopic data (Table 3). The molecular structure along with the atom numbering Scheme is depicted in Figs. 8a and 8b, where the asymmetric unit contains two crystallographically independent molecules and the bond lengths and angles are within normal ranges. The selected bond lengths, bond angles and torsion angles and the hydrogen-bond geometry are given in Tables 4 and S1 (see Table S1 in the Sopporting Information), respectively. The average C-S bond lengths and C-S-C bond angles are 1.787(4) Å and 101.59(19)° (for molecule I) and 1.789(4) Å and 101.26(19)° (for molecule II) (Table S1), respectively. The ligand cavities may play important roles in the complexations and metal-ion selectivities. The intramolecular S1...C5 [6.454(3) Å], S2...C21 [6.603(3) Å],C11...C21 [6.210(3) Å],C5...C15 [6.019(3) Å], C5...C21 [6.068(3) Å], C6...C21 [6.005(3) Å] (in molecule I) and S7...C42 [6.506(4) Å], S8...C26 [6.475(4) Å], S8...C27 [6.004(3) Å], C32...C42[6.064(3) Å], S7C41 [5.990(3) Å], C26...C42 [5.967(3) Å], (in molecule II) distances may indicate the hole sizes of the rings. The planar rings A(C6-C11), B(C15-C20),C(C27-C32) and D(C36-C41) are oriented at dihedral angles of A/B=24.50(13)°, A/C = 11.77(12)°, A/D = 43.56(11)°, B/C $= 15.89(14)^{\circ}$, B/D = 21.40(12)^{\circ} and C/D = 32.29 (12)^{\circ}. In the crystal structure, intermolecular C-H··S interactions (Table 4) link the molecules into infinite chains along the a-axis (see Figure S22 in Supporting Information), while the molecules are stacked

along the a-axis and elongated along the c-axis (see Figure S21 in Supporting Information). 39



Figure 8a. ORTEP-3 [3] drawing (for molecule I) of the title compound with the atomnumbering Scheme. Displacement ellipsoids are drawn at the 50% probability level.



Figure 8b.ORTEB-3 [3] drawing (for molecule II) of the title compound with the atomnumbering Scheme. Displacement ellipsoids are drawn at the 50% probability level.

Empirical formula	$C_{21}H_{18}N_2S_4$		
Colour/shape	colorless/plate		
Formula weight	426.61		
Т (К)	120(2)		
Radiation used, graphite monochr.	Mo K _α (λ = 0.71073 Å)		
Crystal system	monoclinic		
Space group	P 2 ₁ /n		
a (Å)	10.9323 (2)		
b (Å)	16.1929 (3)		
c (Å)	23.1279 (5)		
α(°)	90		
β(°)	97.186 (3)		
χ(°)	90		
V (Å ³)	4062.07 (14)		
z	8		
Absorption coefficient (mm ⁻¹)	0.477		
ρ_{calc} (mg mm ⁻³)	1.395		
Crystal dimensions (mm)	0.09 x 0.19 x 0.24		
θ(Max.) (°)	25.68		
θ(Min.) (°)	2.95		
Reflections measured	7673		
Range of <i>h</i> , <i>k</i> , <i>l</i>	-13 <h 11<="" <="" td=""></h>		
	-19 < <i>k</i> < 19		
	-28 < <i>l</i> < 28		
No of reflections with $I>2\sigma(I)$	4899		
Corrections applied	Lorentz-polarization		
Structure solution	Direct methods		
Treatment of H atoms	Geometric calculations		
No. of parameters var	487		
Goodness-of-fit S	1.044		
$R = F_o - F_c / F_o $	0.0564		
R _w	0.1442		

Table 3. Crystallographic data for Com. 7.

 R_{int} $(\Delta/\rho)_{max}$ (e Å⁻³) 0.0696 0.991

Table 4. Hydrogen-bond geometry (Å, o) for Com.7.

D-H···A	D-H	Н…А	D…A	D-H…A
C21-H21B…S8 ⁱ	0.99	2.67	3.546(4)	148
C42-H42A…S1 ⁱⁱ	0.99	2.84	3.572(4)	131

Symmetry codes: (i) ½ -x, ½ + y, ½ - z, (ii)3/2 -x, -½ + y, ½ - z.

Selected theoretical bond lengths, bond angles and torsion angles of the **Com.7** and **MgPz** compounds computed from B3LYP/6-31G(d) are given in Table S2 (see Table S2 in the Supporting Information) with the experimental data as a supplementary material. The computed bond lengths, bond angles and torsion angles, as shown in Table S2, help us to understand the molecular structure of the **Com.7** and **MgPz** compounds. For example, the mean bond length of the N-C is measured as 1.141 Å while it is computed as 1.165 Å for **Com.7** and 1.336 Å for **MgPz** by using B3LYP/6-31G(d) level. Also, the mean length value of the S-C is measured as 1.7877 Å while it is computed as 1.824 Å for **Com.7** and 1.821 Å for **MgPz** by using B3LYP/6-31G(d) level.

The mean bond angle of the C–S–C is measured as 101.423° it is calculated as 104.133° for **Com.7** and 104.739° for **MgPz** using B3LYP/6-31G(d) level. The mean bond angle of the C–C–C is measured as 112.450° it is calculated as 110.159° for **Com.7** and 110.665° for **MgPz**. The mean bond angle of the N–C–C is measured as 177.725° it is calculated as 177.988° for **Com.7**. It is calculated as 124.345° for **MgPz**. Additionally, the selected dihedral angles for the compounds are also given in Table S2.

As a result, the experimental value of bond lengths, bond angles and torsion angles of the compounds were compared with theoretical method. The correlation ($R^2 = 0.9985$ and $R^2 = 0.9903$) between the experimental and theoretical bond lengths of the **Com.7** and **MgPz** is good, as shown in Figure 9. There is compatibility between experimental and theoretical results for the geometric parameters of the chemical compounds.



Figure 9. The correlation graphs between the experimental and calculated geometric parameters of the **Com.7** and **MgPz** calculated by using B3LYP/6-31G(d).

3. Conclusions

Here, a novel porphyrazinato magnesium (II) complex derived from 7,8-dihydro-6H,14H, 19H-dibenzo[bj][1,12,5,8]tetradithiacyclopentadecine-16,17-dicarbonitrile has been synthesized in a multi-step reaction sequence and characterization. The optimized conditions for some reaction steps such as SNAr (3) reduction (4) and iodination (5) reactions have been achieved. The 15-membered tetrathia macrocycle (7) was synthesized and the X-ray structure of this compound showed that it crystallizes in the monoclinic system with a P2₁/n space group. In addition, we also investigated the geometry optimization of tetrathia macrocycle (7) and magnesium porphyrazine by means of B3LYP method with 6-31G(d) basis set. Some X-ray data such as bond lenghts, bond angles and structure concerning macrocyclic compound were compared with theoretical results in Figure 9. Theoretical calculation of Com.7 and MgPz compounds obtained by using B3LYP/6-31G(d) level are reported here for the first time. It is seen that there is compatibility between experimental and theoretical results for characterizing the compounds. The HOMO and LUMO orbitals of Com.7 and MgPz have also been predicted. Macrocylic precursor compound (7) and metallo porphyrazine (MgPz) containing symmetrically four macrocyclic units provide an opportunity of these compounds for heavy metal extraction, especially soft metals, in extractions from water media to organic phase. Some steps of the synthesis of macrocycle could be completed on green chemistry area.

4. Experimental Section

4.1. General: All organic solvents used were analytical grade and dried over standard drying agent and procedures prior to use.⁴⁰Anhydrous butanol was stored over magnesium butoxide and distilled before. Unless otherwise stated, all reactions were carried out under argon atmosphere in a vacuum line or using standard Schlenk techniques. TLC was performed on Merck aluminum sheets with silica gel 60 F254. Merck silica gel 60 (0.063-0200 mm) was used for column chromatography. Melting points were determined on an electrothermal melting point apparatus in a sealed capillary and are uncorrected. Infrared and UV-vis spectra were recorded with on a spectrometer and on a Shimadzu Perkin Elmer UATR Two UV-1601 spectrophotometer, respectively. ¹H and ¹³C NMR spectra were recorded with a Varian Mercury plus 300 MHz spectrometer. The reported chemical shifts are given relative to $Si(CH_3)_4$ and were locked to the signal of the solvent. Mass spectra of compounds were obtained a Thermo TSQ Quantum Access MAX. LC-MS/MS and in linear modes with average of 50 shots on a Bruker Daltonicis Microflex mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. cis-1,2-Dicyano-1,2-ethylenedithiolate was prepared according to the literature.⁴¹

4.2. X-ray crystallography

Suitable crystals of the title compound was crystallized from ethanol. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K_a radiation (λ =0.71073 Å) at T=120(2) K. Absorption correction by multiscan⁴² was applied. Structure was solved by direct methods and refined by full-matrix least squares against F² using all data.⁴³ All non-H atoms were refined anisotropically. Aromatic and methylene H atoms were positioned geometrically at distances of 0.95 (aromatic) and 0.99 (CH₂) from the parent C atoms; a riding model was used during the refinement process and the U_{iso}(H) values were constrained to be 1.2U_{eq} (for aromatic and methylene carrier atoms).³⁹ The crystallographic data are given in Table 3. CCDC-1499665 for **com.7** contain the supplementary crystallographic data for this paper.

4.3. Theoretical calculations

DFT methods account for electron correlation by estimating the interaction of an electron with the total electron density. DFT orbitals are formed from basis functions like those used in SCF or MP2. The most popular DFT method is B3LYP (Becke3-Parameter method for calculating that part of the molecular energy due to overlapping orbitals plus the Lee–Yang–Parr method of accounting for correlation).⁴⁴ The theoretical calculations were performed to determine whether they are compatible with the experimental and theoretical results.

The molecular structure of the compound was optimized to get the global minima using B3LYP/6-31G(d) level. The same calculation procedure is also used to predict the 1H and 13C NMR chemical shielding constants in gas phase by applying the GIAO-B3LYP. After that, the same basis set and computational method are used for the vibrational spectra of the compound by using the optimized structure. Moreover, TD-DFT/B3LYP/6-31G(d) computations of the compound were used to predict the electronic absorption spectra in gas phase. All the calculations were performed in gas phase by using Gaussian 09. Revision C1 program on TUBITAK clusters.⁴⁵ In addition, GaussView 5.0.9 was used for the visualization of the structure.⁴⁶

4.4. Synthesis

Synthesis of 1,5-Bis(2-formylphenyl)-1,5-dithiapentane (3)

Propane-1,3-dithiol (2.16 g, 20 mmol) was added to a solution of 2-nitro benzaldehyde (6.16 g, 40 mmol) inside a round-bottom flask in dry DMF (50 mL) under argon atmosphere at room temperature. Finally powdered anhydro potassium carbonate (6 g, 43.47 mmol) was added portion-wise and the reaction mixture was stirred at 60 °C for 27 h. The reaction was monitored by a thin layer chromatography [silica gel (chloroform)]. The mixture was filtered off while hot and then cooled to room temperature. The cooled solution was poured into crashed ice (150 g) and resulting mixture was filtered, washed with cooled water and the dried in vacuo. The pale yellow solid product was recrystallized from ethanol that afforded desired compound

inexcellent yield. Yield: 5.65 g (89%), mp. 83-85 °C (lit.data¹: mp.56-57 °C, lit data²: mp.51-53 °C, lit. data³: mp.112-114 °C). ¹H NMR (300 M Hz,CDCl₃): δ 10.36 (s, 2H, HC=O), 7.84 (d, *J* = 7.83 Hz, 2H, ArH), 7.49 (t, *J* = 7.63 Hz, ArH, 2H), 7.41 (d, *J* = 7.83 Hz, 2H, ArH), 7.31 (t, *J* = 7.43 Hz, 2H, ArH), 3.12 (t, *J* = 7.04 Hz, 4H, CH₂S), 2.12-2.06 (m, 2H, CH₂). ¹³C NMR (75.MHz, CDCl₃): δ 191.39, 140.96, 134.12, 133.98, 132.34, 128.23, 125.61, 31.98,27.28. FT-IR (cm⁻¹): 3064 (Ar-H), 2963-2841 (C-H), 1674 (HC=O), 1583, 1558, 1456, 1195, 742. MS (ESI) m/z = 317 [M+1]⁺. Anal. calc. for C₁₇H₁₆O₂S₂: C, 64.55, H, 5.06. Found: C, 64.38; H, 5.20.

Synthesis of 1,5-Bis(2-benzyl alcohol)-1,5-dithiapentane (4)

In a round-bottom flask (25 mL) charged with SiO₂ (0.836 g, 13.92 mmol) and water (0.42 mL) was added and stirred to obtain homogenize mixture. Precursor compound (**3**) (1.32 g, 4.18 mmol) was added to wet SiO₂ and this reaction mixture was stirred for 10 min. NaBH₄ (0.159 g, 4.18 mmol) as a fine powder was then aded. The reaction mixture was turned waxy within 1-2 min. and then dichloro methane (60 mL) was added and stirred at room temperature for overnight. The mixture was filtered, washed with dichloromethane and dried over MgSO₄ and then the solvent was removed to give a pale yellow oily product, which was used without further purification. Yield: 1.14 g (85%) (lit. data⁴: 70%, lit. data⁵: 85%).¹H NMR (300 MHz,CDCl₃): δ 7.36 (d, *J* = 6.65 Hz, 4H, Ar-H), 7.32-7.30 (m, 4H, Ar-H), 4.71 (s, 4H, CH₂OH) 2.99 (t, *J* = 7.04 Hz, 4H, SCH₂), 2.87 (br, 2H, OH), 1.94-1.87 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 140.93, 134.00, 130.05, 128.25, 128.17, 126.74, 63.35, 32.86, 28.32. FT-IR (cm⁻¹): 3308 (O-H), 3057-3014 (Ar-H), 2917-2870 (C-H), 1599, 1439, 1192, 1032, 745. MS (ESI) m/z : 320 [M]⁺. Anal. calc. for C₁₇H₂₀O₂S₂: C, 63.75; H, 6.25. Found: C, 63.59; H, 6.10.

Synthesis of 1,5-Bis(2-iodomethyl)phenyl-1,5-dithiapentane (5)

A round bottom flask which contained compound **4** (1.26 g, 3.94 mmol) and NaI (3.53 g, 23.52 mmol) in dry acetonitrile (50 mL) and which was fitted with a condenser was evacuated, refilled three times with argon and connected to the vacuum line. To a solution of the corresponding alcohol, bromotrimethylsilane (3.57g, 23.36 mmol) was added with continuous stirring. The reaction mixture was stirred at room temperature for 20 min. and monitored by thin layer chromatography [silica gel(chloroform)]. A mixture of dichloromethane and water [100 mL (1:1)] was added to the reaction mixture and the organic phase was further treated with water, saturated Na₂S₂O₃ (20 mL) and water and then dried over MgSO₄. The organic phase was evaporated to dryness under reduced pressure, yielding pale yellow crystal solid. Yield: 1.95 g (92%), mp.73-74 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.35 (d, *J* = 1.57 Hz, 2H, Ar-H), 7.29 (d, *J* = 1.17 Hz, 2H, Ar-H), 7.22 (d, *J* = 1.57 Hz, 2H, Ar-H), 7.13 (d, *J* = 1.56 Hz, 2H, Ar-H), 4.61 (s, 4H, CH₂-I), 3.16 (t, *J* = 7.04 Hz, 4H, CH₂S), 2.08-2.01 (m, 2H, CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 138.78, 135.49, 130.16, 129.82, 128.73, 126.60, 32.32, 28.24, 4.66. FT-IR (cm⁻¹): 3053, 3036, 2952-2941, 1594, 1467, 1150, 1034,

752. MS (ESI) m/z : 541.956 $[M+1]^+$, 413 $[M-I]^+$, 284.9 $[M-2I-2]^+$, 163.2 $[M-C_7H_6SI_2]^+$, 137 $[M-C_8H_8SI_2]^+$. Anal. calc. for $C_{17}H_{18}S_2I_2$: C, 37.79; H, 3.33. Found: C, 37.97; H, 3.17.

Synthesisof 7,8-dihydro-6H,14H,19H-dibenzo[bj][1,12,5,8]tetradithiacyclopentadecine-16,17-dicarbonitrile (7)

A mixture of 1,5-bis(2-iodomethyl)phenyl-1,5-di-thiapentane (2.7 g, 5 mmol) and 1,2dicyano-1,2-ethylenedithiolate disodium salt (0.93 g, 5 mmol) in dry acetonitrile (170 mL) in around-bottom two necked flask was heated and stirred at reflux temperature under argon atmosphere for 24 h. The reaction was monitored by thin layer chromatography [silica gel (chloroform:hexane) (1:1)] and then allowed to cool to room temperature. The solvent was evaporated to dryness under reduced pressure and the residue was solidified by stirring water (80 ml) at room temperature overnight. The brown solid was filtered and the solids washed with water and then dried in vacuo. The solid was chromatographed on silica gel [(chloroform:hexane)(1:1)] and recrystallized from ethanol to give 7 as a yellow crystals. Yield: 0.4 g (19%), mp.156-158 °C. ¹H-NMR (300 MHz, CDCl₃): δ 7.34 (d, J = 7.83 Hz, 2H, Ar-H₆), 7.21 (d, J = 7.43 Hz, 2H, Ar-H₅), 7.15 (t, J = 6.85 Hz, 2H, Ar-H₄), 7.08 (t, J = 6.85 Hz, 2H, Ar-H₃), 4.27 (s, 4H, Ar-CH₂S, H₉), 2.97 (t, J = 7.85 Hz, 4H, CH₂S, H₂), 1.96-1.92 (m, 2H, CH₂, H₁). ¹³C- NMR (75 MHz, CDCl₃): δ 136.99 (C₈), 134.39 (C₇), 132.69 (C₅), 130.29 (C₄), 128.83 (C₆), 127.53 (C₃), 123.19 (C₁₀), 112.80 (C₁₁), 38.31 (C₉), 34.58 (C₂), 30.09 (C₁). FT-IR (cm⁻¹): 3064, 3012, 2967-2920, 2208, 1588, 1469, 1421, 1260, 1167, 734, 663. MS (ESI) m/z: 426.57 [M]⁺. Anal. calc. for $C_{21}H_{18}N_2S_4$. C, 59.15; H, 4.22; N, 6.57. Found: C, 59.06; H, 4.30; N, 6.47.

Synthesis of Magnesium porphyrazine (MgPz)

Mg powder (0.0148 g,0.616 mmol) and I_2 (one small crystal) and 1-butanol was (5 mL) charged in a Schlenk system connected with vacuum line under argon atmosphere. The reaction mixture was refluxed and stirred for 12 h till all metal was dissolved. The suspension was cooled to room temperature and dicyano compound (6) (0.426 g, 1 mmol) in dry butanol (2 mL) was added and then the mixture was further heated at reflux temperature for 28 h. The reaction was monitored by thin layer chromatography [silica gel (chloroform:hexane) (1:1)]. The deep dark blue suspension was cooled to room temperature, filtered and washed with methanol. The solution was concentrated in vacuo and the residue was purified by column chromatography over silica gel [(chloroform: hexane) (1:1)] to obtain dark blue crystals. Yield: 0.10 g (23%), mp>300 °C. ¹H-NMR (300 MHz, CDCl₃+DMSO-d₆): δ 7.42-7.40 (m, 8H, Ar-H), 7.12-7.10 (m, 8H, Ar-H), 7.04-7.01 (m, 8H, Ar-H), 6.78-6.75 (m, 8H, Ar-H), 5.40 (s, 16H, Ar-CH₂S), 3.22-3.18 (m, 16H, CH₂S), 1.98-1.95 (m, 8H, CH₂). ¹³C- NMR (75 MHz, CDCl₃): δ 140.05, 134.73, 134.34, 130.32, 128.07, 127.68, 115.75, 38.82, 35.02, 28.53. FT-IR (cm⁻¹): 3053, 3003, 2963-2911, 1626, 1586, 1467, 1439, 1418, 1291, 1209, 1034, 757. MS (ESI) m/z: 1728.16 [M]⁺. Anal. calc. for C₈₄H₇₂N₈S₁₆Mg. C,

58.33; H, 4.16; N, 6.48. Found: C, 58.44; H, 4.07; N, 6.59. UV-vis (CHCl₃): λ_{max} (log ϵ): 685 (5.25), 625 (4.76), 519 (4.39), 383 (5.12).

Supporting Information

Selected crystallographic data, experimental bond lengths (Å), bond angles (o) and torsion angles (o) for **Com.7**. Calculated structural data for **Com.7** and selected bond lengths (Å), bond angles (o) and torsion angles (o) for **Com.7** and **MgPz**. A partial packing diagram of **Com.7**. Hydrogen bonds are shown as dashed lines. A partial packing diagram viewed down the a-axis. Copies of the ¹H, ¹³C NMR, IR, MS spectral data of all compounds and UV-vis data of **MgPz**.

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Highlights

•The convenient synthesis of substituted benzyl alcohol from substituted aldehyde form in green chemistry conditions.

•Synthesis of iodinated derivative of subtituted benzyl alcohol with excellent yield, short reaction time, simple work up and fairly mild conditions.

•X-ray characterization of 15-membered S₄ macrocycle.

•The compatibility between experimental and theoretical results of S₄-macrocycle and MgPz.