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Synthesis, Characterization, and Theoretical Studies on Some Metallophthalocyanines With Octakis Phenoxyacetamide Substituents

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The synthesis of substituted metallophthalocyanines bearing phenoxyacetamide moieties was achieved by cyclotetramerization of 1,2-bis(phenoxyacetamide)-4,5-dicyanobenzene in the presence of metal (Zn (4), Mg (5), Ni (6)) salts. These compounds were purified by several techniques such as crystallization, column chromatography, and wash with different solvents. The new compounds were characterized by elemental analysis, IR, ¹H-NMR, and UV-Vis spectral data. The ground-state geometries of the complexes were optimized using density functional theory (DFT) methods at B3LYP/6-31G (d, p) level. The results of thermal analysis of novel phthalocyanines 4–6 have also been reported herein.

Keywords DFT, metal complexes, phenoxyacetamide, phthalocyanines, phthalonitrile, thermal stability

INTRODUCTION

Phthalocyanine is an intensely blue-green–colored macrocyclic compound that is widely used in dyeing.^[1–3] Phthalocyanines form coordination complexes with most elements of the periodic table. These complexes are also intensely colored and also are used as dyes or pigments.

Phthalocyanines have been investigated for many decades as active components in such diverse fields as media for optical data storage, electrochromic, optical limiting devices, multistage-redox-dependent fluorophores, photosensitisers, chemical inertness, very high thermal stability, electrical conductivity, photoconductivity, catalytic activity, and medicinal therapeutic agents.^[4–8] Moreover, phthalocyanine compounds have been investigated as donor materials in molecular electronics (e.g., organic field-effect transistors^[9] and metal phthalocyanines have long been examined as catalysts for redox reactions). Areas of interest are the oxygen reduction reaction and the sweetening of gas streams by removal of hydrogen sulfide.

Phthalocyanine forms upon heating phthalic acid derivatives that contain nitrogen functional groups. Classical precursors are phthalonitrile and diiminoisoindole. However, different synthesis strategies have been used to prepared phthalocyanine derivatives, which are mainly based on the periphery covalent linkings by using functional groups.^[1,10]

Our continuing efforts on the synthesis of novel phthalocyanines with macrocyclic substituents have enabled us to reach products with hexadeca tert-butyl,^[11] phenoxyacetamide,^[12] macrocycles. The nature of substituents can strongly influence the essential parameters of a phthalocyanine, such as its solubility, thermal stability, electronic absorption, and chemical sensing properties. In the present article, we report the synthesis, electronic, and thermal properties of metallophthalocyanines bearing octakis phenoxyacetamide substituents.

EXPERIMENTAL

Electronic spectra were recorded on a Hitachi U-2900 Spectrophotometer (Van YYU, Central Laboratory, Turkey). Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer (Van YYU, Central Laboratory, Turkey) in KBr pellets. Melting points were measured on an electrothermal apparatus. ¹H NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer (Trabzon KTU Central Laboratory, Turkey) with tetramethylsilane as internal standard. Elemental analyses results were found in good agreement with calculated values. Thermal experimental was performed in a SETARAM TG/DTA/DSC-16 instrument (Van YYU, Central Laboratory, Turkey). All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego^[13] and the solvents were stored over molecular sieves (4 Å).

Preparation of 1, 2-Bis (phenoxyacetamide)-4, 5-dicyanobenzene (3)

4,5-dichloro-1, 2-dicyanobenzene (0.985 g, 0.005 mol) was dissolved in dimethyl sulfoxide (DMSO) (20 cm³) under nitrogen atmosphere and 4-acetamidophenol (1.51 g, 0.01 mol) was added. After stirring for 15 min at room temperature, finely ground anhydrous potassium carbonate (2.8 g, 0.02 mol) was added in portions in a 2-h period with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature

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FIG. 1. B3LYP/6-31G(d) optimized structures of the three metallocyanines and a representative side view (color figure available online).

for 24 h. Then, the mixture was poured into 200 mL water, and precipitate was filtered off, washed successively with water and little acetone, and dried *in vacuo* (50°C). The yield was 1.55 g (72.7%). Anal. Calcd. (%) for C₂₄H₁₈N₄O₄: C, 67, 60; H, 4.25; N, 13, 14. Found (%): C, 67, 57; H, 4.27; N, 13, 15. IR spectrum (cm⁻¹): 3298, 3069, 2864, 2802, 2232, 1666, 1590, 1253, 1016, 854, 506. ¹H NMR (DMSO-d₆) δ , ppm: 8.08(NH), 7.78–7.17 (Ar-H), 2.35(CH₃).

Preparation of

octaphenoxyacetamidephthalocyaninatozinc (II) (4)

Compound 3 (0.106 g, 0.25 mmol) and excess ZnCl₂ were powdered in a quartz crucible and heated in a sealed glass tube for 7 min under nitrogen atmosphere at 330°C. After cooling to room temperature, a green-colored reaction product was obtained. The product was washed with water, EtOH, acetone, THF. DMF (2 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding EtOH. The precipitate was filtered and washed with EtOH. Compound **4** is soluble in DMF, DMSO.

The yield of compound **4**: 0.030 g (27.27%). Anal. Calcd. for C₉₆H₇₂N₁₆O₁₆Zn_: C, 65, 10; H, 4.10; N, 12, 65%. Found: C, 65, 12; H, 4.08; N, 12, 64%. IR spectrum (cm⁻¹):3259, 1667, 1503, 1202, 889, 661, 448, UV-vis (DMF) λ max nm (log ε): 682(4.85), 617(3.65).

Preparation of octaphenoxyacetamidephthalocyaninatomagnesium (II) (5)

Compound **3** (0.106 g, 0.25 mmol) and excess MgCl₂.6H₂O were powdered in a quartz crucible and heated in a sealed glass tube for 7 min under nitrogen atmosphere at 330° C. After cooling to room temperature, a green-colored reaction product was obtained. The product was washed with EtOH, CHCl₃, and ethyl acetate. DMF (2 mL) was added to the residue in order

to dissolve the product. The reaction mixture was precipitated by adding EtOH. The precipitate was filtered and washed with EtOH. Compound **5** is soluble in DMF, DMSO.

The yield of **5**: 0.022 g (20.37%) Anal. Calcd. (%) for $C_{96}H_{72}N_{16}O_{16}Mg$: C,66,65; H,4.19; N,12,95. Found (%): C, 66, 66; H, 4.17; N, 12, 96. IR spectrum (cm⁻¹): 3260, 1723, 1503, 661, 449. UV-Vis (DMF) λ max nm (log ε):680(5.24), 614(4.41), 360(4.45).

Preparation of

octaphenoxyacetamidephthalocyaninatonickel (II) (6)

Compound **3** (0.106 g, 0.25 mmol) and excess NiCl₂ were powdered in a quartz crucible and heated in a sealed glass tube for 7 min under nitrogen atmosphere at 330°C. After cooling to room temperature, a green-colored reaction product was obtained. The product was washed with EtOH, hot EtOH, and THF. DMF (2 mL) was added to the residue in order to dissolve the product. The reaction mixture was precipitated by adding EtOH. Compound 6 is soluble in DMF and DMSO.

The yield of 6: 0.025 g (22.72 %). Anal. Calcd. (%) for $C_{96}H_{72}N_{16}O_{16}Ni : C,65,35; H,4.11; N,12,70.$ Found (%): C, 65, 33; H, 4.13; N, 12, 72. IR spectrum (cm⁻¹): 3294, 1665, 1502, 1399, 1252, 1013, 847, 507. UV-Vis (DMF) λ max nm (log ε): 673(5.06), 637(5.00), 346(518), 336(5.21), 320(5.22).

COMPUTATIONAL DETAILS

The molecular structures were geometry optimized using density functional theory at B3LYP/6-31G (d, p) level with no symmetry constrains. The Gaussian 03 package program has been used during all computational calculations.^[14] The vibrational analysis for each metal complex does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. The normal mode analysis was performed for 3N-6 vibrational degrees of freedom, *N* being the number of atoms forming the system.

The time-dependent density functional theory (TD-DFT) calculation has been used to compute the vertical excitation energies, oscillator strengths (f), and excited state compositions in terms of excitations between the occupied and virtual orbitals for metal complexes.^[15,16] In this study, the TD-DFT method with the same basis set has been performed to obtain absorption wavelengths and the oscillation strength (f) within visible to near-UV region. For the goal of approaching available experimental results, we have performed 100 allowed transitions (nstates = 100) in our TD-DFT calculation process.

RESULTS AND DISCUSSION

Our key starting compound **3** was obtained by the reaction between 4,5-dichloro-1, 2-dicyanobenzene **2** and 4acetamidophenol 1 in dry dimethylsulfoxide (DMSO) in the presence of dry K_2CO_3 . The synthesis of metal complexes **4–6** have been achieved by heating **3** with ZnCl₂, MgCl₂.6H₂O and NiCl₂ metal salts under nitrogen atmosphere (Scheme 1). The metal coordinates with four equivalents of the ligand to give the final corresponding metallophthalocyanine. Melting points of the compounds **4–6** were found to be higher than 300° C. Moreover, solubility tests revealed that these phthalocyanines **4–6** are not soluble in common solvents but soluble in DMF and DMSO.

Spectral data of the synthesized compounds are consistent with the proposed structures. Comparison of the IR spectral data clearly indicated the formation of compound **3** by the appearance of new absorption bands at $3297-3267 \text{ cm}^{-1}$ (NH), 2232 cm^{-1} (CN), $1666-1590 \text{ cm}^{-1}$ (C=C), 1204 cm^{-1} (Ar-O-Ar). After conversion of the compound **3** into the phthalocyanines (**4–6**), the sharp peak for the CN vibration around 2232 cm^{-1} disappeared.

The ¹H NMR spectrum of **3** exhibited NH at 10.08(s, 2H), aromatic protons at 8.05 (dd, J = 8.73, Ar-H), 7.71 (s, Ar-H), 7.70(s, Ar-H), 7.66 (dd, J = 8.73, Ar-H), 7.31 (dd, J = 8.73, Ar-H), 7.11 (dd, J = 8.73, Ar-H), and 2.03 (s, 6H, -CH₃).

The geometry optimized structures and the Mulliken charge^[17] distribution in the heart of the present complexes are shown in Figures 1 and 2, respectively. The complexes are computed to be square planar at the phthalocyanine moiety; however, the phenoxyacetamide substituents were oriented perpendicular to the main plane and got almost parallel positioning to one another. One phenoxyacetamide aligned up in the space the other down such that the steric hinderence have been minimized and the most stable ground state structures have been obtained. As seen in Figure 2 the net charges on Zn, Mg, and Ni are 1.022,



FIG. 2. Mulliken charge distribution for Zn, Mg, Ni metallocyanines, respectively (color figure available online).



SCH. 1. The route for the synthesis of metallophthalocyanines.

1.258, and 0.885, respectively, being lower than the formal charge +2. It is a consequence of charge donation from coordinating nitrogen atoms. All donor atoms of the ligands possess negative charge development. The coordinating nitrogen atoms are almost twice more negative than the connecting nitrogen atoms, which might be a result of absence of imino hydrogen atom. The expected -1 formal charge on these atoms decreased absolutely to -0.687 (-0.750 and -0.672) upon coordination to the corresponding positively charged metal atom.

The UV–vis spectra of the phthalocyanine **4–6** in DMF showed characteristic Q band absorptions between 673 and 682 nm, which were attributed to the π - π * transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in UV region at 346–360 nm were observed due to transition from the deeper π levels to the LUMO (Figure 3).



FIG. 3. Absorption spectrum of 4-6 in DMF.



FIG. 4. The molecular orbitals involved in electronic transitions (color figure available online).

The spectra showed monomeric behavior evidenced by a single Q band, typical of metallated phthalocyanines compounds for **4–6** in DMF which depict the monomeric nature of the these complexes in this solvent.^[18] Geometry optimized structures have been subjected to TD-DFT calculations with the same basis set to predict electronic spectra. Transition energies and molecular orbital energies and schemes have been predicted for singlet state excitations. The characteristic bands appeared at 668–680 nm for the series **4–6**. Calculated molecular orbital en-

ergies indicate HOMO and LUMO to be responsible for these bands. Three-dimensional HOMO and LUMO energy schemes are shown in Figure 4. The carbon atoms of the central periphery contribute most to HOMOs of the complexes; however, contributions from outer atoms cannot be ignored. On the other hand, LUMOs of the three systems are mainly composed of both the carbon and nitrogen atoms of the phthalocyanine moiety together with some contribution form the metal atoms in the cases of Zn and Ni.

Compound	Initial dec temp (åC)	Main dec. temp (åC)
4	400	610
5	370	680
6	410	620

It is well known that phthalocyanines exhibit excellent thermal stability. According to thermal analyses, temperatures of $450-600^{\circ}$ C are the limit of thermal treatment under inert gas.^[19,20] The thermal properties of the octakis phenoxyacetamide substituted phthalocyanine derivatives **4–6** were investigated by thermogravimetric analysis. The initial and main decomposition temperatures are given in Table 1.

Phthalocyanine derivatives **4–6** substituted octakis phenoxyacetamide groups, showed a weight loss corresponding to moisture at 100–140°C. The initial and extensive decompositions occur at *ca*. 410–420°C and 610–680°C. The thermal decomposition of **4** in nitrogen atmosphere was observed to be very slow. 17% mass loss of compound **4** was found at 1095°C (Figure 5). Moreover, mass losses of 7% and 49% were observed for **5** and **6**, respectively. These temperatures are higher than those found for different organic substituted groups containing phthalocyanine complexes.^[21] Thus, the substitution of phthalocyanine core with phenoxyacetamide groups increases the thermal stability of the present phthalocyanines complexes **4–6** significantly, when compared with other phthalocyanines substituted with different organic groups.

The previous trend conform relatively higher stability of these complexes in open air in the order 5 > 4 > 6. DTA results revealed that all degradation steps are exothermic in nature. As seen Figure 5, there exist an increasing decomposition in the material between 300 and 800°C. In comparison with the substituted phthalocyanine derivatives containing different types of



FIG. 5. TG /DTA curves of 4 (color figure available online).

organic groups, octakis phenoxyacetamide substituted phthalocyanine complexes **4–6** are found to be thermally more stable. Thus, phenoxyacetamide groups on phthalocyanine ring have a stabilizing effect on the thermal property. In conclusion, the phthalocyanines reported in this work can be considered as efficient candidates for potential applications that require thermal durability.

CONCLUSIONS

In the present study, the synthesis of Zn, Mg, and Ni metallophthalocyanines with octakis phenoxyacetamide substituents have been reported. The structural characterizations of the compounds have been performed by various spectroscopic data. Additionally, some structural and electronic information obtained from theoretical calculations at the level of B3LYP/6-31G (d, p) have been revealed. Theoretical calculations indicated that the substituents oriented perpendicular to the main plane to minimize the steric repulsion. Last, the results of the thermal analysis showed that these novel complexes are more durable at higher temperatures than their previously reported counterparts.

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