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Novel phthalocyanines containing substituted salicyclic hydrazone-1, 3-thiazole moieties: Microwave-assisted synthesis, spectroscopic characterization, X-ray structure and thermal characterization

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ABSTRACT

Novel, metal-free and metallo(Cu, Co, Ni, Zn, Pb and Mn)phthalocyanine compounds were synthesized by exposure to microwave irradiation and the products purified. The newly prepared compounds were characterized using elemental analyses, IR, $^1H/^{13}C$ NMR, $^1H–^1H$ COSY measurements, MS, UV–vis spectroscopy and DTA/TG analysis. The electronic spectra exhibited an intense $\pi \rightarrow \pi^*$ transition with characteristic Q and B bands of the phthalocyanine core, as expected. All decomposition products obtained from DTA/TG analysis were identified; it was found that the thermal stability of each phthalocyanine compound followed the order: MnPc < Metal-free < ZnPc < PbPc < CuPc < CoPc < NiPc.

1. Introduction

First discovered about 102 years ago [1], phthalocyanines (pc's) have never lost their popularity. Pcs enjoy manifold applications in fields such as electrophotography, photovoltaic and solar cells, molecular electronics, Langmuir–Blodgett films, electrochromic display devices, gas sensors, NLO, optical discs and sensitizers in photodynamic therapy of cancer (PDT) [2,3]. Although the well-known insolubility of peripherally unsubstituted metal phthalocyanines in common organic solvents can restrict their use [4], the introduction of substituents at peripheral sites modifies this solubility. Considerable efforts have been made to generate novel Pc derivatives possessing enhanced properties, such as higher solubility in common organic solvents [5]. This behaviour becomes very important especially in PDT applications [6–18], since lipophilic phthalocyanines have high tumor affinity because of their solubility in the serum media [19]. For these reasons, attempts to synthesize novel PC's offer promise.

Aromatic heterocyclic compounds containing nitrogen and sulfur have important industrial uses. Thiazole, a five-membered ring heterocycle, is an important species of this type and enjoys widespread use for manufacturing biocides, fungicides, dyes and pharmaceuticals, treatment of inflammation, hypertension, bacterial and HIV infections. The thiazole moiety represents an important part of vitamin B1 (thiamine) and epothilone, a potent anti-cancer drug. In general, thiazoles are well represented in biomolecules. Thiazoles are characterized by a larger delocalisation of the π-electrons than that obtained for the corresponding oxazoles and, therefore, possess superior aromatic character [20–23].

In the last decade, microwave energy has attracted interest as an alternative to traditional heating, because microwave heating possesses inherent advantages namely, it is direct, selective and rapid; microwave-assisted synthesis can result in increased yields and lowered reaction times [24–26]. The authors have previously synthesized phthalocyanines using microwave irradiation [27–29].

This work concerns the synthesis, characterization and structural investigation of both metal-free Pc's and Cu(II), Co(II), Ni(II), Zn(II), Pb(II) and Mn(II) metallophthalocyanines, which contain sulfur, nitrogen and oxygen donor atom, macrocyclic moieties. The

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solubility of the compounds in common organic solvents can be anticipated to offer benefits for many fields.

2. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [30]. Ethyl (2*E*)-2-[(2*Z*)-(2-hydroxybenzylidene) hydrazono]-3,4-dimethyl-2,3-dihydro-1,3-thiazole-5-carboxylate **2** was obtained from condensation of 2-hydroxy-benzaldehyde *N*-methylthiosemicarbazone **1** [31] and ethyl-2-chloro-acetoacetate **1a** (purchased by Fluka), and 4-nitrophthalonitrile **3** [32] was prepared according to the literature. ^{1}H NMR, ^{13}C NMR and ^{1}H-^{1}H COSY spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer in KBr pellets. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer equipped with pyridine–methanol as solvent. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument; their values agreed with the calculated ones. UV–vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. The DTA/TG measurements were made with Seiko-II Exstar 6000 analyzer. Beko MD 1500, 2.45 MHz domestic microwave oven, was used in all synthesis of phthalocyanines, except for metal-free. Melting points were measured on an electrothermal apparatus and were uncorrected.

2.1. Synthesis

2.1.1. Ethyl (2E)-2-[(2Z)-(2-hydroxybenzylidene) hydrazono]-3, 4-dimethyl-2,3-dihydro-1,3-thiazole-5-carboxylate 2

Ethyl-2-chloro-acetoacetate **1a** (12.34 g, 0.075 mol) was added to a solution of compound **1** (15.68 g, 0.075 mol) in absolute ethanol (0.2 L). After the mixture was refluxed and stirred for 80 h, the solution was filtered and the solid obtained was washed with water, ethyl alcohol, diethyl ether, successively. The precipitated solid was recrystallized from appropriate solvent [Chloroform–petroleum ether (1:2)] to obtain the desired compound. Yield: 4.9 g, (20.5%), mp: 179–180 °C.

Anal. Calc. for $C_{15}H_{17}N_3O_3S$: C, 56.41; H, 5.37; N, 13.16. Found: C, 56.43; H, 5.38; N, 13.14. IR (KBr tablet) υ_{max}/cm^{-1}: 3413 (-OH), 3043 (Ar–CH), 1728 (C=O), 1605–1542 (CH=N/C=C), 1314 (C–N), 1270 (C–OH), 1098 (C–O), 1049, 619 (C–S).

^{1}H NMR ($CDCl_3$), (δ: ppm): 11.26 (s, 1H, OH/D_2O exchangeable), 8.44 (s, 1H, CH = N), 7.31–7.27 (m, 1H/Ar–H_{11}), 7.02 (d, 1H/Ar–H_9, $J = 7.92$ Hz), 6.98–6.93 (dd, 1H/Ar–H_8, $J = 8.06$ and 1.02 Hz), 6.89–6.85 (dd, 1H/Ar–H_{10}, $J = 7.94$ and 1.03 Hz), 4.30–4.20 (q, 2H/OCH_2, $J = 7.05$ Hz), 3.45 (s, 3H/NCH_3), 2.54 (s, 3H/CCH_3), 1.32 (t, 3H/$OCCH_3$, $J = 7.39$ Hz).

^{13}C NMR ($CDCl_3$), (δ: ppm): 165.26 (C_{14}), 160.33 (C_{13}), 151.88 (C_{17}), 147.21 (C_7), 146.30 (C_{16}), 132.51 (C_9), 129.16 (C_{11}), 125.50 (C_{12}), 120.88 (C_{10}), 117.59 (C_8), 101.66 (C_{15}), 60.37 (–CH_2), 37.34 (C_{21}), 14.21 (C_{19}), 12.49 (C_{20}).

MS (ESI), (*m*/*z*): Calculated: 319.10; Found: 320.15 $[M+1]^+$.

2.1.2. Ethyl (2E)-2-{(2Z)-[2-(3,4-dicyanophenoxy)benzylidene] hydrazono}-3,4-dimethyl-2,3-dihydro-1,3-thiazole-5-carboxylate 4

A mixture of 4-nitrophthalonitrile **3** (1.63 g, 0.94 × 10^{-2} mol) and dry DMF (0.015 L) was charged into a 0.2 L three-necked flask and stirred at room temperature under nitrogen inert atmosphere. Ethyl (2*E*)-2-[(2*Z*)-(2-hydroxybenzylidene) hydrazono]-3,4-dimethyl-2,3-dihydro- 1,3-thiazole-5-carboxylate **2** (3.00 g, 0.94 × 10^{-2} mol) was added to the solution and the temperature was increased up to 55–60 °C. Powdered K_2CO_3 (3.84 g, 2.78 × 10^{-2} mol) was added to the system in eight equal portions at 15 min intervals with efficient stirring and the reaction system was stirred at the same temperature for 5 days. Aliquots were taken and checked periodically for completeness of the reactions and observed by thin layer chromatography (TLC) (chloroform). The reaction system was cooled and poured into ice-water and then mixed for 12 h. The mixture was filtered and dried in vacuum over P_2O_5 for 4 h and recystallized from ethanol to give light yellow crystalline powder. Yield: 3.28 g, (78.4%), mp: 225–230 °C.

Anal. Calc. for $C_{23}H_{19}N_5O_3S$: C, 62.01; H, 4.30; N, 15.72. Found: C, 62.18; H, 4.17; N, 15.43. IR (KBr tablet) υ_{max}/cm^{-1}: 3032 (Ar–CH), 2228 (C≡N), 1688 (C=O), 1593–1527 (CH = N/C=C), 1327 (C–N), 1085 (C–O), 1047, 619 (C–S).

^{1}H NMR ($CDCl_3$), (δ: ppm): 8.43 (s, 1H, CH=N), 8.19 (d, 1H/Ar–H_4, $J = 7.72$ Hz), 7.80 (d, 1H/Ar–H_{11}, $J = 8.39$ Hz), 7.60–7.21 (m, 3H/Ar–$H_{1,5,9}$) 6.97 (d, 1H/Ar–H_{10}, $J = 8.39$ Hz), 6.68 (d, 1H/Ar–H_8, $J = 8.30$ Hz), 4.29–4.20 (q, 2H/OCH_2, $J = 7.05$ Hz), 3.61 (s, 3H/NCH_3), 2.45 (s, 3H/CCH_3), 1.38 (t, 3H/$OCCH_3$, $J = 7.39$ Hz).

^{13}C NMR ($CDCl_3$), (δ: ppm): 167.52 (C_{14}), 161.29 (C_{13}), 161.06 (C_6), 150.98 (C_{17}), 148.22 (C_7), 146.34 (C_{16}), 136.19 (C_4), 131.57 (C_9), 128.14 (C_{11}), 127.07 (C_1), 126.51 (C12), 122.12 (C_5), 121.82 (C_{10}), 120.97 (C_2), 116.55 (C_8), 115.76 (C≡N), 107.83 (C_3), 101.62 (C_{15}), 60.35 (–CH_2), 39.34 (C_{21}), 14.14 (C_{19}), 12.44 (C_{20}).

MS (ESI), (*m*/*z*): Calculated: 445.12; Found: 446.26 $[M+1]^+$.

2.1.3. Metal-free phthalocyanine 5

A standart Schlenk tube was charged with (0.2 g, 0.45 × 10^{-3} mol) of **4**, 5 ml of dry *n*-hegzanol and (0.069 × 10^{-3} L, 0.45 × 10^{-3} mol) of 1,8-diazabisiklo[5.4.0]undek-7-en (DBU) under a nitrogen atmosphere and degassed several times. The temparature was gradually increased up to 90 °C and the flask was degassed again with nitrogen. Then the reaction mixture was stirred at 145–150 °C for 24 h. Then, the reaction mixture was cooled and evaporated to dryness. The remaining dark green solid was stirred with 0.025 L diethyl ether–ethanol mixture, filtered and dried in vacuum over P_2O_5. Purification of the solid product was accomplished by column chromatography with basic aluminum oxide (Type-I) [chloroform/methanol (1:0.033) and chloroform/methanol (9:1) as eluents, respectively] to give dark green yield. Yield: 0.15 g, (75% – raw yield); yield of second fraction corresponding to metal-free **5**: 0.061 g, (30.64%), mp>300 °C (decomposition).

Anal. Calc. for $C_{92}H_{78}N_{20}O_{12}S_4$: C, 61.94; H, 4.41; N, 15.70. Found: C, 61.70; H, 4.63; N, 15.89. IR (KBr tablet) υ_{max}/cm^{-1}: 3292 (–NH), 3060 (Ar–CH), 1692–1645 (υC=O/δNH), 1595–1526 (CH=N/C=C), 1319 (C–N), 1086 (C–O), 1045, 620 (C–S).

^{1}H NMR ($CDCl_3$), (δ: ppm): 9.17 (s, 4H, CH = N), 8.81 (d, 4H/Ar–H_4, $J = 7.02$ Hz), 8.66 (d, 4H/Ar–H_{11}, $J = 8.00$ Hz), 8.40–7.60 (m, 12H/Ar–$H_{1,5,9}$) 7.51 (d, 4H/Ar–H_{10}, $J = 8.01$ Hz), 7.18 (d, 4H/Ar–H_8, $J = 8.01$ Hz), 4.20–4.06 (q, 8H/OCH_2, $J = 7.21$ Hz), 3.37 (s, 12H/NCH_3), 2.51 (s, 12H/CCH_3), 1.39 (t, 12H/$OCCH_3$, $J = 7.11$ Hz).

^{13}C NMR ($CDCl_3$), (δ: ppm): 173.81 (Ca), 164.90 (C_{14}), 163.86 (C_{13}), 162.24 (C_6), 156.91 (C_{17}), 156.11 (C_7), 147.73 (C_{16}), 147.01 (C_4), 143.89 (C_9), 131.13 (C_{11}), 127.31 (C1), 124.68 (C_{12}), 121.23 (C_5), 118.11 (C_{10}), 113.96 (C_2), 111.81 (C_8), 108.23 (C_3), 104.91 (C_{15}), 65.20 (–CH_2), 34.74 (C_{21}), 14.33 (C_{19}), 13.01 (C_{20}).

UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 248(5.23), 306(5.16), 368(5.24), 404(5.15), 615(4.78), 647(4.86), 675(5.17), 707(5.24). MS (ESI), (*m*/*z*): Calculated: 1782.50; Found: 1783.16 $[M + 1]^+$.

2.1.4. The general procedure for synthesis of metallophthalocyanines 6–11

A mixture of compound **4** (0.15 g, 3.36 × 10^{-4} mol), related anhydrous MCl_2 (M = Cu (0.0114 g, 0.84 × 10^{-4} mol); Co (0.011 g, 0.85 × 10^{-4} mol); Mn (0.014 g, 0.84 × 10^{-4} mol)) and $M(CH_3COO)_2$

(M = Ni (0.015 g, 0.84×10^{-4} mol); Zn (0.015 g, 0.85×10^{-4} mol); Pb (0.021 g, 0.056×10^{-3} mol)), dry DMAE (5×10^{-3} L) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.51×10^{-4} L, 3.36×10^{-4} mol) was irradiated in a microwave oven at 175 °C, 350 W for 6–10 min. Then it was diluted with hot ethanol (ca. 0.03 L) and stirred for 12 h. The raw product was filtered and then washed with hot ethanol, water, diethyl ether and dried in vacuum over P_2O_5. Purification of the solid products was accomplished by column chromatography with basic aluminium oxide (Type-I) [chloroform/methanol (1:0.033) and chloroform/methanol (9:1) as eluents, respectively] to give dark green yield. The chemical and physical spectral characteristics of these products **6**–**11** are given below.

*2.1.4.1. Cu (II) phthalocyanine **6**.* Microwave time for CuPc was 6 min. Yield: 0.13 g, (83.6%), mp >300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Cu$: C, 59.87; H, 4.15; N, 15.18; Cu, 3.44. Found: C, 60.01; H, 4.41; N, 15.37; Cu, 3.21. IR (KBr tablet) υ_{max}/cm^{-1}: 3062(Ar–CH), 1691(C=O), 1595–1525 (CH=N/C=C), 1320 (C–N), 1085 (C–O), 1045, 622 (C–S). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 232(4.98), 251(5.19), 300(5.20), 314(5.18), 332(5.18), 354(5.19), 368(5.19), 495(5.16), 639(4.78), 691(5.24). MS (ESI), (m/z): Calculated: 1843.41; Found: 1845.61 $[M + 2]^+$.

*2.1.4.2. Co(II) phthalocyanine **7**.* Microwave time for CoPc was 8 min. Yield: 0.096 g, (61.9%), mp > 300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Co$: C, 60.02; H, 4.16; N, 15.22; Co, 3.20. Found: C, 59.80; H, 4.39; N, 15.45; Co, 3.52. IR (KBr tablet) υ_{max}/cm^{-1}: 3064(Ar–CH), 1695(C=O), 1595–1527 (CH=N/C=C), 1319 (C–N), 1086 (C–O), 1041, 610 (C–S). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 227(5.06), 252(5.25), 309(5.16), 367(5.21), 610(4.78), 688(5.26). MS (ESI), (m/z): Calculated: 1839.42; Found: 1839.01 $[M]^+$.

*2.1.4.3. Ni(II) phthalocyanine **8**.* Microwave time for NiPc was 6 min. Yield: 0.088 g, (56.8%), mp>300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Ni$: C, 60.03; H, 4.16; N, 15.22; Ni, 3.19. Found: C, 60.27; H, 4.04; N, 15.56; Ni, 3.40. IR (KBr tablet) υ_{max}/cm^{-1}: 3061(Ar–CH), 1692(C=O), 1595–1530 (CH=N/C=C), 1319 (C–N), 1083 (C–O), 1048, 611 (C–S).

^{1}H NMR ($CDCl_3$), (δ: ppm): 9.06 (s, 4H, CH = N), 8.84–6.83 (bm, 24H/Ar–$H_{1,4,5,9,10,11}$), 6.65 (d, 4H/Ar–H_8, J = 8.03 Hz), 4.16 (bs, 8H/OCH_2), 3.49 (s, 12H/NCH_3), 2.49 (s, 12H/CCH_3), 1.20 (bs, 12H/$OCCH_3$).

^{13}C NMR ($CDCl_3$), (δ:ppm): 173.28 (Ca), 168.13 (C_{14}), 162.98 (C_{13}), 161.60 (C_6), 155.52 (C_{17}), 154.42 (C_7), 149.89 (C_{16}), 148.50 (C_4), 140.08 (C_9), 131.52 (C_{11}), 129.52 (C_1), 127.22 (C_{12}), 127.01 (C_5), 126.79 (C_{10}), 126.42 (C_2), 126.18 (C_8), 114.39 (C_3), 114.29 (C_{15}), 60.26 (–CH_2), 34.19 (C_{21}), 14.04 (C_{19}), 12.37 (C_{20}). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 259(5.25), 305(5.17), 367(5.23), 395(5.15), 620(4.78), 680(5.21). MS (ESI), (m/z): Calculated: 1838.42; Found: 1839.72 $[M+1]^+$.

*2.1.4.4. Zn(II) phthalocyanine **9**.* Microwave time for ZnPc was 8 min. Yield: 0.097 g, (62.4%), mp > 300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Zn$: C, 59.81; H, 4.15; N, 15.16; Zn, 3.54. Found: C, 59.91; H, 4.27; N, 15.24; Zn, 3.62. IR (KBr tablet) υ_{max}/cm^{-1}: 3059 (Ar–CH), 1695 (C=O), 1596–1527 (CH=N/C=C), 1322 (C–N), 1086 (C–O), 1045, 614 (C–S). ^{1}H NMR ($CDCl_3$), (δ: ppm): 8.78 (s, 4H, CH = N), 8.76–6.60 (bm, 28H/Ar–$H_{1,4,5,8,9,10,11}$), 4.20 (q, 8H/OCH_2, J = 7.19 Hz), 3.39 (s, 12H/NCH_3), 2.43 (s, 12H/CCH_3), 1.21 (t, 12H/$OCCH_3$, J = 7.33 Hz).

^{13}C NMR ($CDCl_3$), (δ:ppm): 168.95 (Ca), 168.32 (C_{14}), 162.84 (C_{13}), 161.16 (C_6), 152.65 (C_{17}), 152.07 (C_7), 148.38 (C_{16}), 146.15 (C_4), 141.34 (C_9), 131.69 (C_{11}), 127.47 (C1), 127.06 (C_{12}), 126.27 (C_5), 125.35 (C_{10}), 121.87 (C_2), 121.58 (C_8), 110.19 (C_3), 101.62 (C_{15}), 60.43 (–CH_2), 38.92 (C_{21}), 14.12 (C_{19}), 12.48 (C_{20}). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 223(4.95), 257(5.27), 294(5.22), 316(5.23), 357(5.25), 389(5.15), 406(5.17), 621(4.83), 690(5.26). MS (ESI), (m/z): Calculated: 1844.42; Found: 1846.18 $[M + 2]^+$.

*2.1.4.5. Pb(II) phthalocyanine **10**.* Microwave time for PbPc was 10 min. Yield: 0.054 g, (48.3%), mp > 300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Pb$: C, 55.55; H, 3.85; N, 14.08; Pb, 10.42. Found: C, 52.48; H, 4.30; N, 13.44; Pb, 10.62. IR (KBr tablet) υ_{max}/cm^{-1}: 3059 (Ar–CH), 1694 (C=O), 1593–1525 (CH=N/C=C), 1319 (C–N), 1080 (C–O), 1045, 613 (C–S). ^{1}H NMR ($CDCl_3$), (δ: ppm): 9.21 (s, 4H, CH = N), 8.88–6.80 (bm, 28H/Ar–$H_{1,4,5,8,9,10,11}$), 4.21 (bs, 8H/OCH_2), 3.33 (s, 12H/NCH_3), 2.42 (s, 12H/CCH_3), 1.20 (bs, 12H/$OCCH_3$). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 254(5.24), 304(5.22), 368(5.20), 619(4.72), 687(5.27). MS (ESI), (m/z): Calculated: 1988.46; Found: 1989.53 $[M + 1]^+$.

*2.1.4.6. Mn(II) phthalocyanine **11**.* Microwave time for MnPc was 8 min. Yield: 0.14 g, (90.5%), mp > 300 °C (decomposition).

Anal. Calc. for $C_{92}H_{76}N_{20}O_{12}S_4Mn$: C, 60.15; H, 4.17; N, 15.25; Mn, 2.99. Found: C, 60.11; H, 4.07; N, 15.31; Mn, 3.20. IR (KBr tablet) υ_{max}/cm^{-1}: 3062 (Ar–CH), 1699 (C=O), 1595–1528 (CH=N/C=C), 1322 (C–N), 1082 (C–O), 1048, 617 (C–S). UV–vis (chloroform): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 265(5.27), 301(5.27), 317(5.28), 364(5.29), 393(5.25), 690(4.78), 738(5.27).

MS (ESI), (m/z): Calculated: 1835.42; Found: 1858.12 $[M + Na]^+$.

3. Results and discussion

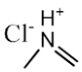
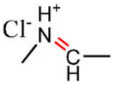
3.1. Outlook of synthesized compounds

The preparation of substituted salicyclic hydrazone-1,3-thiazole schiff base **2**, substituted phthalonitrile **4**, target metal-free pc **5** and metallophthalocyanines **6**–**11**, is shown in Fig. 1. The structures of novel compounds were characterized by combination of ^{1}H/^{13}C NMR, ^{1}H–^{1}H COSY, IR, UV–vis, elemental analysis and MS spectral data while X-ray diffraction method was used for compound **2** in addition to all spectroscopic methods.

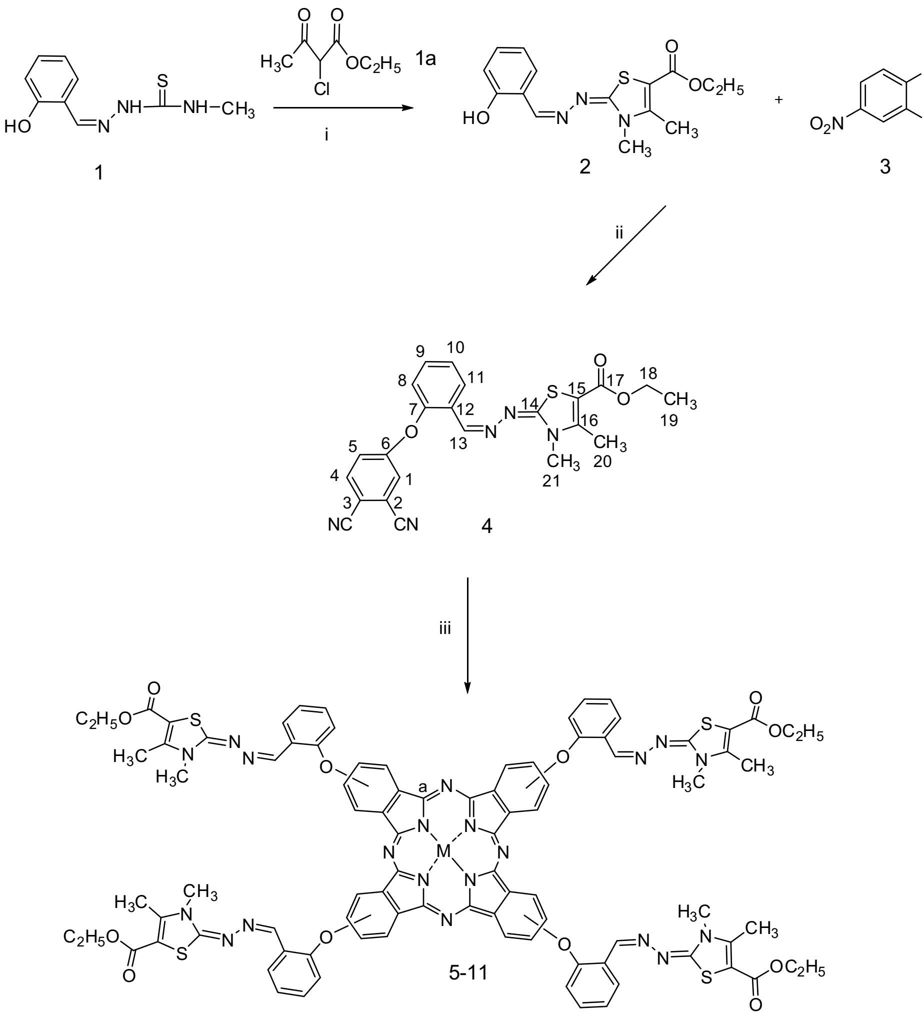
3.2. Spectroscopic characterization via complementary techniques

3.2.1. Synthesis of precursor 2

Functionalized salicyclic hydrazone-1,3-thiazoled schiff base **2** was typically synthesized via the ring-closure reaction of **1** and ethyl-2-chloro-acetoacetate **1a** in a high yield-(20.5%) [7]. This procedure consists of four steps (Fig. 2);

i. the attack to acidic carbon of ethyl-2-chloro-acetoacetate of thiosemicarbazone sulfur,
ii. the existing of C–S bond and  form,
iii. via tautomerism, the migration on one of the carbonylies of ethyl-2-chloro-acetoacetate of the double  bond,
iv. finally, the existing of substituted-1,3-thiazole ring with five members.

The IR spectra were used to identify substituents disappearing or appearing on the periphery of related compounds. In the IR spectrum of **2**, **s**tretching vibration peaks of two different adjacent –NH groups (3267–3203 cm^{-1} corresponds to starting reactant **1**) and of C=S group (1255–1201 cm^{-1}) were not obvious, indicating amino groups in 2-hydroxy-benzaldehyde *N*-methylthiosemicarbazone skeletal **1** have been converted into tertiary amine and



i: dry Ethanol/reflux
ii: dry DMF, dry K_2CO_3, N_2, 55-60°C
iii: classical method, 24 h, DMAE/DBU, 175°C, Metal free
microwave, 350 W, 6 min, DMAE/DBU, 175°C, anhydrous $CuCl_2$
microwave, 350 W, 8 min, DMAE/DBU, 175°C, anhydrous $CoCl_2$
microwave, 350 W, 6 min, DMAE/DBU, 175°C, anhydrous $Ni(CH_3COO)_2$
microwave, 350 W, 8 min, DMAE/DBU, 175°C, anhydrous $Zn(CH_3COO)_2$
microwave, 350 W, 10 min, DMAE/DBU, 175°C, anhydrous $Pb(CH_3COO)_2$
microwave, 350 W, 8 min, DMAE/DBU, 175°C, anhydrous $MnCl_2$

Compound	5	6	7	8	9	10	11
M	2H	Cu	Co	Ni	Zn	Pb	Mn

Fig. 1. The synthesis of metal-free and metallophthalocyanines.

hydrazonic thiazole via the ring-closure. In addition, a new band at 1728 cm^{-1} was also appeared corresponding to C=O group, indicative of condensation reaction. The rest of the spectrum of **2** was similar closely those of **1** and **1a** involving the characteristic vibrations of aliphatic, azomethine and phenolic groups. ^1H NMR spectrum of **2** was almost identical to **1** and **1a**, with only small changes in shifts. The difference between spectra of compound **1** and substituted schiff base **2** is seen clearly to arise from the absence of secondary amines –NH at ca. 11.33 ppm. Salicyclic benzene protons $H_{8,9}$ and H_{10} are observed as doublets of doublet (6.98–6.93 ppm), doublet (7.02 ppm) and doublets of doublet (6.89–6.85 ppm), respectively [33,34] (Fig. 3). H_{11} aromatic proton appeared as multiplet form at 7.31–7.27 ppm due to the closeness to the azomethine proton. The down-field shifting of H_{11} and H_9 protons in comparison with the others is due to the strengthening of mesomeric effect of different electronegative atoms (oxygen and nitrogen) towards H_8 and H_{10} protons, as expected [35]. In addition, the metylene protons generally show the behaviour of AB spin system. Interestingly, as presented by D. Maciejewska et al. and L. Schröder et al. [36,37], the methylenic protons of **2** are observed as a triplet peak with A_2 spin system at 4.30–4.20 ppm. This behaviour indicates these protons are isochronous protons in magnetic field. ^{13}C NMR spectrum of **2** also clearly indicates the presence of C=O, C–S and CH_2 group bands at 151.88, 101.66 and 60.37 ppm, respectively. The MS mass spectrum of **2** shows a molecular ion peak at $m/z = 320.15$ $[M+1]^+$, supporting the proposed formula for this compound.

3.2.2. Synthesis of substituted dinitrile 4

The compound **4** was obtained from the reaction of **2** with 4-nitrophthalonitrile **3** in dry K_2CO_3/dry DMF under N_2 atmosphere at 55–60 °C in schlenk system, for 5 days. This is accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with **2** [15–18,29]. Similarly, comparison of the IR spectral data clearly indicated the formation of compound **4** by the disappearence of the O-H bands of **2** at 3413 and 1270 cm^{-1}

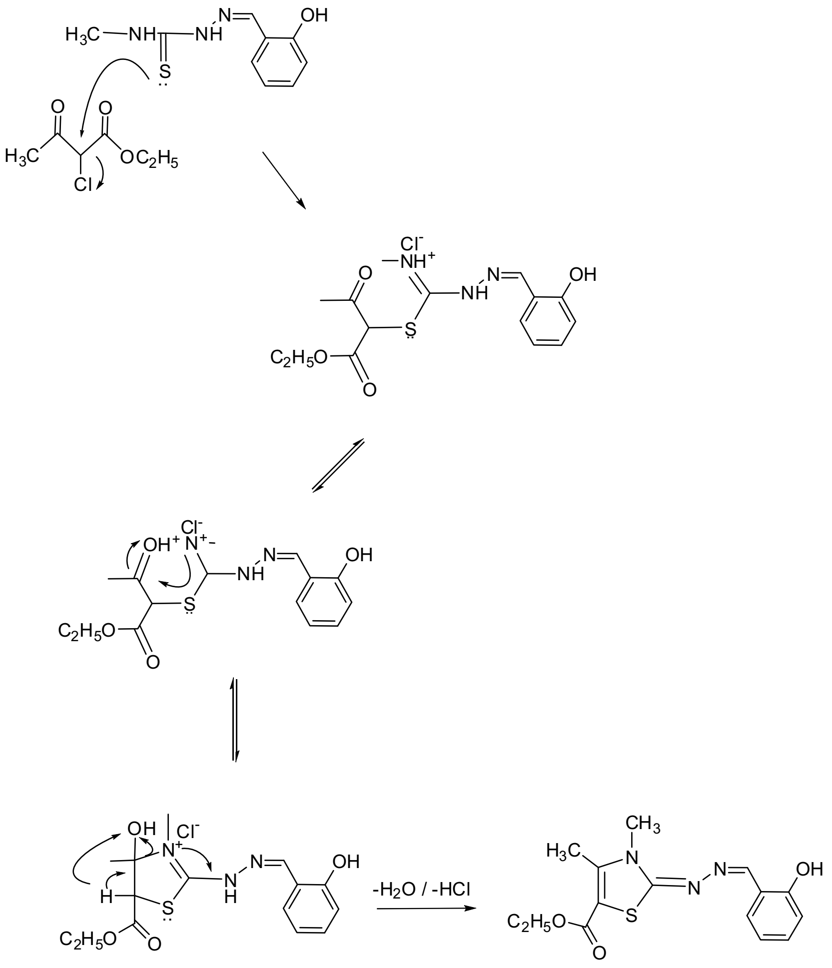


Fig. 2. The synthetic route to precursor **2**.

and those of NO_2 bands of **3** at 1519 and 1333 cm^{-1}, and by the appearance of a new absorption at 2228 cm^{-1} ($C{\equiv}N$). Besides, in the ^1H NMR spectrum of **4,** disappearance of the resonance belonging to salicyclic –OH group at 11.26 ppm confirmed the existence of expected compound **4**. While the ^1H NMR spectra of **2** and **4** are mostly similar, the proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon atom in **4** at $\delta = 115.76$ ppm. At the same time, ^1H NMR spectral assignments are also supported via ^1H–^1H COSY experiment. ^1H–^1H COSY is more helpful to get detailed information about which protons correlate with certain protons. As can be seen from the ^1H–^1H COSY (Fig. 4), H_8 aromatic proton with vicinal coupling constant $J = 8.30$ Hz (as doublet) at 6.68 ppm correlates with H_9 aromatic proton at 7.60–7.21 ppm (as multiplet form), H_{10} aromatic proton with vicinal coupling constant $J = 8.39$ Hz (as doublet) at 6.97 ppm couples to the H_{11} aromatic proton at 7.80 ppm as doublet, H_4 proton with doublet form at 8.19 ppm couples to H_5 proton, and also the methylenic protons H_{18} at 4.29–4.20 ppm correlate with methyl protons H_{19} at 1.38 ppm as A_2 spin system, respectively, supporting the ^1H NMR spectrum data [38]. In addition, the MS mass spectrum of **4** shows a molecular ion peak at $m/z = 446.26$ $[M + 1]^+$, supporting the proposed formula for this compound.

*3.2.3. Syntheses of metal-free 5 and metallophthalocyanines **6–11***

In microwave oven, all attempts performed to obtain the metal-free **5** resulted in failure. So, the metal-free derivative (H_2Pc) **5** was obtained directly by the reaction of substituted phthalonitrile **4** with dry *n*-hexanol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [29]. In the case of metal salts, however, all metallophthalocyanines were prepared by self-condensation of phthalonitrile based on 1,3-thiazole **4** [27–29]. The reactions were carried out in refluxing N,N-dimethylaminoethanol (DMAE), affording the desired metallophthalocyanines. Further more, in the microwave-assisted method, the reactions of **6–11** were accomplished in DMAE/DBU mixtures at 350 W/10 min for Pb(II), 350 W/8 min for Co(II), Zn(II) and Mn(II), and 350 W/6 min for Cu(II) and Ni(II). The desired products were purified by basic silica gel column chromatography using a gradient of chloroform/methanol (1:0.033) and chloroform/methanol (9:1) as eluents. The solubility of the phthalocyanines was moderate in common organic solvents such as ethyl acetate, acetone, tetrahydrofurane and ethanol.

The IR spectrum of metal-free phthalocyanine **5** shows known classical –NH band (inner –NH) at 3292 cm^{-1} as indicated in previous reports [11–14,27–29]. The rest of the spectrum of **5** was similar to that of **4** except for $C{\equiv}N$ group in **4**. In the ^1H NMR spectrum of **5**, the typical shielding of inner core protons could not be observed due to the probable strong aggregation (especially for our molecules, due to multiplicities of the numbers of aromatic benzenes) of the molecules [39]. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave a significant absorbance characteristic of the proposed structure. Further more, the MS mass spectrum of **5** shows a molecular ion peak at $m/z = 1783.16$ $[M + 1]^+$, supporting the proposed formula for this compound.

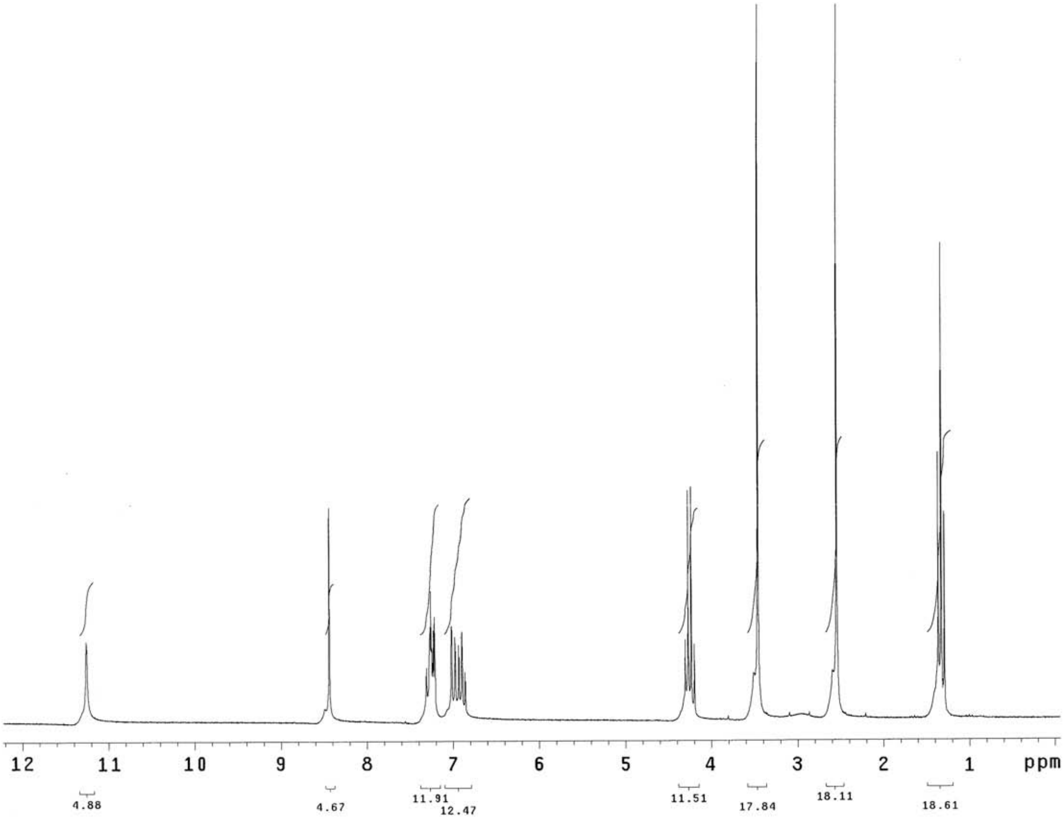


Fig. 3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

The metallophthalocyanines **6**–**11** were obtained from substituted cyano derivative **4** and corresponding anhydrous metal salts $CuCl_2$, $CoCl_2$, $Ni(CH_3COO)_2$, $Zn(CH_3COO)_2$, $Pb(CH_3COO)_2$ and $MnCl_2$ respectively, with microwave irradiation in DMAE for 6–10 min. In the IR spectra of all metallophthalocyanines, the disappearence of strong C≡N stretching vibration of **4** at ca. 2228 cm^{-1} was an enough evidence for the formation of Metal-Pcs. Due to the paramagnetic nature of **6**, **7** and **11**, ^{1}H NMR spectra of these compounds could not be taken. In addition, in the ^{1}H NMR spectra of NiPc and PbPc, the protons pertaining to OCH_2 and $OCCH_3$ could not be well defined due to the strong aggregation in phthalocyanine units and probable maskings of peripheral substituents to each other. These could be observed as broad singlet form instead. In the mass spectra of compounds **6**–**11**, the molecular ion peaks were observed at $m/z = 1845.61$ $[M+2]^+$ for Cu(II), 1839.01 $[M]^+$ for Co(II), 1839.72 $[M+1]^+$ for Ni(II), 1846.18 $[M+2]^+$ for Zn (II), 1989.53 $[M+1]^+$ for Pb(II) and 1858.12 $[M+Na]^+$ for Mn(II). These peak values confirmed the proposed structures.

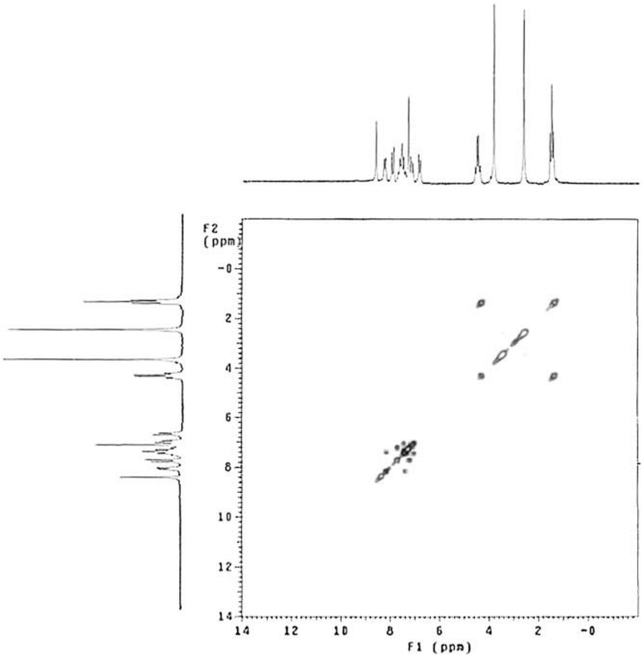


Fig. 4. ^{1}H–^{1}H COSY spectrum of compound **4** in $CDCl_3$.

3.3. UV–Vis absorption spectra

In general, phthalocyanines show typical electronic spectra with two strong absorption regions, the B band (ca. 300–500 nm) corresponding to the UV region and the Q band (ca. 600–750 nm) corresponding to the visible region [15–18,29]. The Q band absorptions of **5** in chloroform at $\lambda = 707$, 675 nm, and 647 and 615 nm as shoulders and the other absorptions (as B bands) at 404, 368, 306 and 248 nm are consistent with the results obtained for previous phthalocyanines [15–18,29,40,41], and which have been ascribed to the deeper $\pi \rightarrow \pi^*$ levels of LUMO transitions (Fig. 5a). As can be also shown from the spectrum, the splitting of Q band absorption of **5** to Q_x and Q_y bands can be attributed to the fact that the symmetry of metal-free phthalocyanine is nondegenerate (D_{2h}) [15–18,29]. Additionally, an increase in the concentration leads to aggregation which is easily monitored by the position of the Q band shifting to shorter wavelengths, and to a decrease in molar absorption coefficient [15–18,29,35].

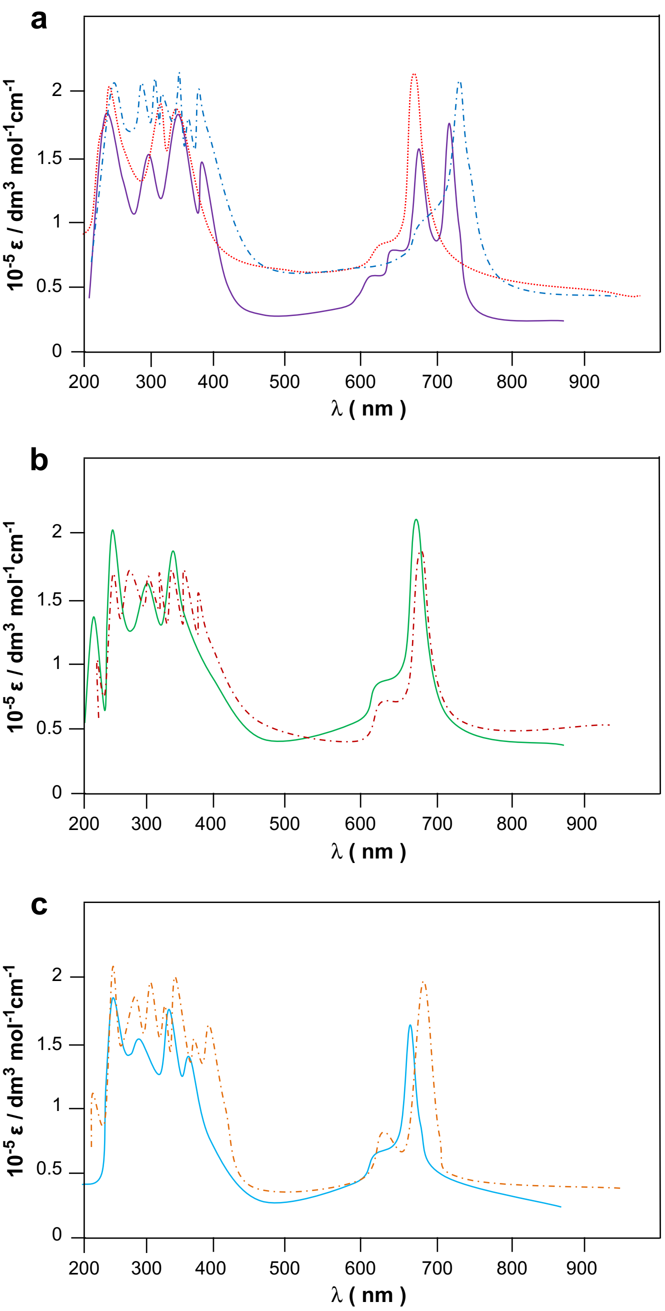


Fig. 5. a. UV–vis spectra of compounds Mn (–.–.), Pb (….) and Free (—) as blue, red and purple coloured lines respectively in $CHCl_3$. b. UV–vis spectra of compounds Cu (–.–.) and Co (—) as dark red and green coloured lines respectively in $CHCl_3$. c. UV–vis spectra of compounds Zn(–.–.) and Ni(—) as dark orange and light blue coloured lines respectively in $CHCl_3$.

The UV–vis absorption spectra of metallophthalocyanines **6**–**11** are given in Fig. 5a–c. These compounds showed the expected absorptions at the main peaks of the Q and B bands appearing at $\lambda = 691$, 639 nm (corresponds to degenerate D_{4h} symmetry) and between 495 and 232 nm (corresponds to B region) for Cu(II) (Fig. 5b), 688, 610 nm and between 367 and 227 nm for Co(II) (Fig. 5b), 680, 620 nm and between 395 and 259 nm for Ni(II) (Fig. 5c), 690, 621 nm and between 406 and 223 nm for Zn(II) (Fig. 5c), 687, 619 nm and between 368 and 254 nm for Pb(II) (Fig. 5a), and 738, 690 nm and between 393 and 265 nm for Mn(II) (Fig. 5a), respectively. These results were typical for metal complexes of substituted and unsubstituted Pcs with D_{4h} symmetry [15–18,29,40–42].

Table 1
Thermal properties of all phthalocyanines.

Compound	Initial decomposition temp. (°C)	Main decomposition temp. (°C)
5	222	353
6	292	365
7	293	363
8	299	369
9	231	362
10	284	344
11	161	343

3.4. *DTA/TG characterization*

Thermal properties of the metal-free and metallophthalocyanines were investigated by DTA/TG methods. It is well known that phthalocyanine unit is resistant to thermal oxidation [43]. One can also be seen DTA thermograms of all of the phthalocyanines from Supplementary material. DTA curves exhibited exothermic changes for compounds **5**–**11** studied in the region investigated [44]; it means that there was no melting point for any of the phthalocyanines. The initial decomposition temperature decreased in the order: **11** < **5** < **9** < **10** < **6** < **7** < **8** (Table 1). Pb containing phthalocyanine **10** rapidly decomposed while Co, Cu, Ni, Zn, Metal-free and Mn phthalocyanines showed better thermal stability under working conditions. These results are partially in agreement with the literature [45]. According to the DTA data (see Supplementary material), decomposition consists of two stages for all phthalocyanines. The first step in the decomposition started at ca. 45–222.4 °C for metal-free, ca. 45–291.7 °C for CuPc, ca. 45–293 °C for CoPc, ca. 45–298.7 °C for NiPc, ca. 45–230.7 °C for ZnPc, ca. 45–283.6 °C for PbPc and ca. 45–161 °C for MnPc, respectively. Then, the second step in the decomposition (the main decomposition) occurred at 353.2 °C for metal-free, 364.7 °C for CuPc, 362.9 °C for CoPc, 368.9 °C for NiPc, 361.5 °C for ZnPc, 343.5 °C for PbPc and 342.9 °C for MnPc, respectively. These correspond to the loss and fragmentation of one unit of the peripheral environment of the phthalocyanine molecule. For instance, for metal-free pc, the organic group corresponding to $C_{23}H_{19}N_3O_3S$ peripheral part departed with an estimated mass loss of 23.4% (calcd. mass loss 23.39%); for CuPc, a $C_6H_5NO_2S$ group at peripheral part corresponding to one fourth of the ionized organic group left with an estimated mass loss of 33.41% (calcd. mass loss 33.59%); for CoPc, similarly, a $C_5H_2NO_2S$ unit corresponding to one fourth of the ionized organic group lost with an estimated mass loss

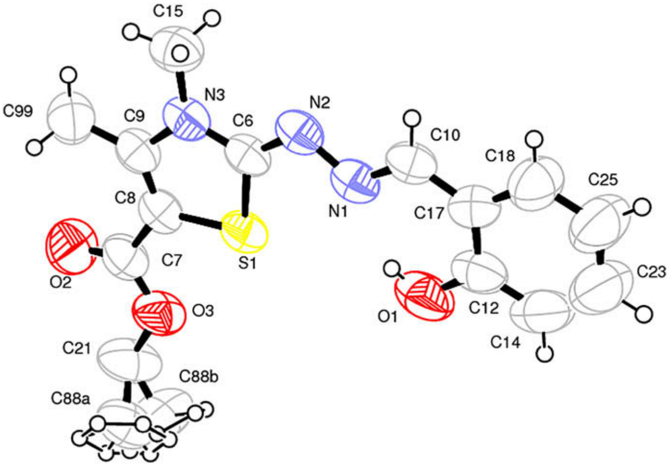


Fig. 6. Ortep III diagram of the title compound **2**.

Table 2
Crystal and experimental data.

Formula: $C_{15}H_{15}N_3O_3S$
Formula weight: 317.36
Crystal system: orthorhombic
Space group: *Pbca*
$Z = 8$
$a = 7.9333(2)$ Å
$b = 20.1408(8)$ Å
$c = 20.6080(6)$ Å
$\alpha = \beta = \gamma = 90^\circ$, and $V = 3292.81(18)$ Å^3,
No. of reflections used = 27 879
$2\theta_{max} = 60^\circ$ MoK_α
$R = 0.073$
$(\Delta/\sigma)_{max} = 0.000$
$(\Delta/\rho)_{max} = 0.300$ eÅ^{-3}
$(\Delta\rho)_{min} = -0.174$ eÅ^{-3}
$F(000) = 1328$
$\mu = 0.211$ mm^{-1}
Measurement: STOE IPDS II
Program system: STOE X-RED
Structure determination: Direct methods
Refinement: Full matrix

of 29.9% (calcd. mass loss 30.2%); in case of NiPc, the leaving group with observed mass loss of 38.1% could not be identified; for ZnPc, $C_8H_{11}N_2O_2S$ part taking up one fourth of the ionized organic group separated with an estimated mass loss of 43.3% (calcd. mass loss 43.2%); for PbPc, a $C_5H_6NO_2S$ corresponding to one fourth of the ionized organic group left with an estimated mass loss of 29% (calcd. mass loss 28.96%); finally, for MnPc, all data were in comparison with the results of CoPc.

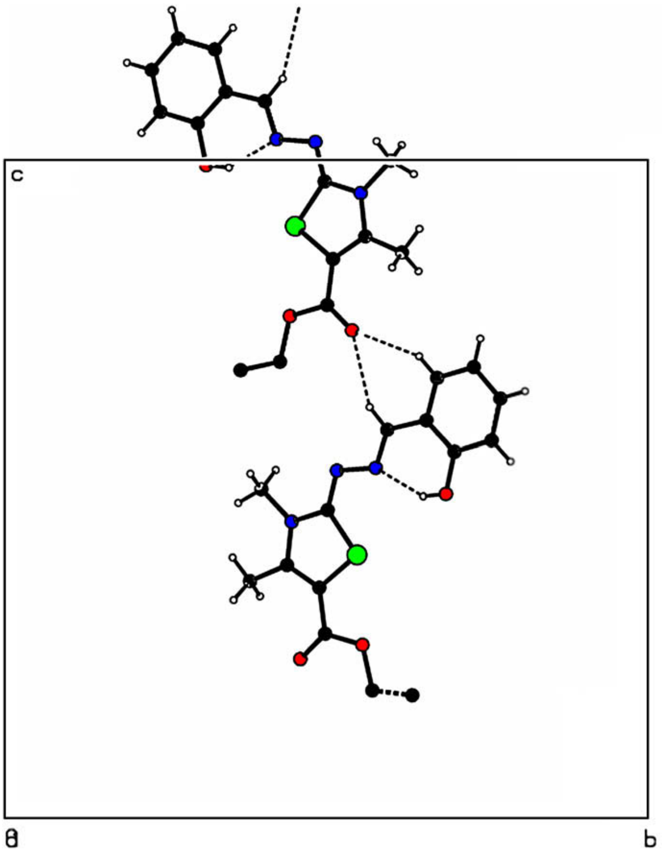


Fig. 7. Packing diagram of the title compound **2** along the *a* axes.

4. X-ray structure of compound 2

The crystal structure of the title compound, $C_{15}H_{15}N_3O_3S$ **2**, was determined by single crystal X-ray diffraction technique, Fig. 6. The title compound crystallizes in the orthorhombic space group *Pbca* with the following unit–cell parameters: $a = 7.9333(2)$ Å, $b = 20.1408(8)$ Å, $c = 20.6080(6)$ Å, $\alpha = \beta = \gamma = 90^\circ$, and V = 3292.81(18) Å^3, crystallographic data is shown in Table 2.

The molecular data were collected on a Stoe IPDS II [46] diffractometer. All diffraction measurements were performed at room temperature (293 K) using monochromatic MoK_α radiation. For the title compound data collection: X-AREA [47]; cell refinement: X-AREA; data reduction: X-RED32 [46]; program was used to solve structure: SHELXS97 [47]; program was used to refine structure: SHELXL97 [47]; molecular figures: ORTEP III [48]; publication software: WinGX [49] and PARST [50] were used. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares procedures on F^2, using SHELXL-97 computer program belonging to the WinGX software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were refined using a riding model.

The high values of the displacement parameters of the C atom of the methyl group attached the carboxylate indicated possible disorder of this group. Following sequence of the refinements and difference Fourier syntheses, disordered atom C_{88} was recognized in 52(2):48(2) ratio in the methyl group. Their atomic parameters

Table 3
Selected bond distances (Å), bond angles (°) and dihedral angles (°) for **2**.

Bond distances (Å)		Bond angles (°)		Dihedral angles (°)	
S_1–C_6	1.734(3)	C_6–S1–C_8	90.28(14)	C_6–N2–N_1–C_{10}	−179.5(2)
S_1–C_8	1.756(3)	C_6–N3–C_9	120.6(2)	N_1–N2–C_6–N_3	−178.5(2)
N_3–C_6	1.372(4)	C_6–N3–C_{15}	115.1(2)	N_1–N2–C_6–S_1	0.5(3)
N_3–C_9	1.386(4)	C_9–N3–C_{15}	124.3(2)	C_9–N3–C_6–N_2	−177.8(2)
N_3–C_{15}	1.467(3)	C_6–N2–N_1	110.2(2)	C_{15}–N3–C_6–N_2	−1.5(4)
N_2–C_6	1.296(3)	C_{10}–N1–N_2	114.6(2)	C_9–N3–C_6–S_1	−1.3(3)
N_2–N_1	1.398(3)	C_7–O3–C_{21}	116.9(3)	C_{15}–N3–C_6–S_1	179.33(18)
N_1–C_{10}	1.282(3)	N_2–C6–N_3	122.2(2)	C_8–S1–C_6–N_2	−178.3(2)
O_3–C_7	1.327(4)	N_2–C6–S_1	127.4(2)	C_8–S1–C_6–N_3	0.85(19)
O_3–C_{21}	1.464(4)	N_3–C6–S_1	110.36(19)	C_{21}–O3–C_7–O_2	−1.3(5)
C_7–O_2	1.198(4)	O_2–C7–O_3	123.1(3)	C_{21}–O3–C_7–C_8	−179.9(3)
C_7–C_8	1.457(4)	O_2–C7–C_8	125.7(3)	O_2–C7–C_8–C_9	−4.7(5)
C_8–C_9	1.352(4)	O_3–C7–C_8	111.1(3)	O_3–C7–C_8–C_9	173.8(3)
C_{10}–C_{17}	1.435(4)	C_9–C8–C_7	127.2(3)	O_2–C7–C_8–S_1	175.9(3)
C_{10}–H_{10}	0.93	C_9–C8–S_1	112.3(2)	O_3–C7–C_8–S_1	−5.5(3)
C_{12}–O_1	1.358(4)	C_7–C8–S_1		C_6–S1–C_8–C_9	−0.2(2)
C_{12}–C_{14}	1.395(6)	C_8–C9–N_3	120.5(2)	C_6–S1–C_8–C_7	179.2(2)
C_{12}–C_{17}	1.397(4)	C_8–C9–C_{99}	111.9(2)	C_7–C8–C_9–N_3	−179.9(2)
O_1–H_1	0.82	N_3–C9–C_{99}	128.3(3)	S_1–C8–C_9–N_3	−0.5(3)
C_{14}–C_{23}	1.361(7)	N_1–C10–C_{17}	119.8(3)	C_7–C8–C_9–C_{99}	−0.4(5)
C_{14}–H_{14}	0.93	N_1–C10–H_{10}	122.9(2)	S_1–C8–C_9–C_{99}	179.0(2)
C_{17}–C_{18}	1.398(5)	O_1–C12–C_{14}	118.6	C_6–N3–C_9–C_8	1.2(3)
C_{18}–C_{25}	0.93	O_1–C12–C_{17}	119.1(3)	C_{15}–N3–C_9–C_8	−179.5(2)
C_{18}–H_{18}	1.377(5)	C_{14}–C12–C_{17}	120.7(3)	C_6–N3–C_9–C_{99}	−178.3(2)
C_{23}–C_{25}	1.358(7)	C_{12}–O1–H_1	120.1(4)	C_{15}–N3–C_9–C_{99}	1.0(4)
C_{23}–H_{23}	0.93	C_{23}–C14–C_{12}	109.5	N_2–N1–C_{10}–C_{17}	−178.7(2)
C_{25}–H_{25}	0.93	C_{23}–C14–H_{14}	119.8(4)	O_1–C12–C_{14}–C_{23}	−178.9(4)
		C_{12}–C17–C_{18}	120.1	C_{17}–C12–C_{14}–C_{23}	1.0(6)
		C_{12}–C17–C_{10}	117.5(3)	O_1–C12–C_{17}–C_{18}	179.5(3)
		C_{18}–C17–C_{10}	123.3(3)	C_{14}–C12–C_{17}–C_{18}	−0.4(5)
		C_{25}–C18–C_{17}	119.2(3)	O_1–C12–C_{17}–C_{10}	1.1(4)
		C_{88B}–C21–C_{88A}	121.7(4)	C_{14}–C12–C_{17}–C_{10}	−178.8(3)
		C_{88B}–C21–O_3	37(2)	N_1–C10–C_{17}–C_{12}	−2.9(4)
		C_{88A}–C_{21}–O_3	109.1(8)	N_1–C10–C_{17}–C_{18}	178.7(3)
		C_{25}–C23–C_{14}	111.5(6)	C_{12}–C17–C_{18}–C_{25}	−0.4(6)
		C_{14}–C23–H_{23}	121.6(4)	C_{10}–C17–C_{18}–C_{25}	178.1(4)
		C_{18}–C25–H_{25}	119.2	C_7–O3–C21–C_{88B}	166(3)
		C_9–C99–H_{99A}	120.4	C_7–O3–C_{21}–C_{88A}	126.6(13)
		H_{88A}–C_{88A}–H_{88D}	109.5	C_{12}–C14–C_{23}–C_{25}	−0.9(7)
		H_{88C}–C_{88A}–H_{88D}	141.1	C_{14}–C23–C_{25}–C_{18}	0.2(8)
			56.3	C_{17}–C18–C_{25}–C_{23}	0.5(7)

Table 4
Hydrogen-bond geometry (Å) in **2**.

Hydrogen-bond geometry (Å) in **2**				
$D{-}H\cdots A$	$D{-}H$	$H\cdots A$	$D\cdots A$	$D{-}H\cdots A$
$O_1{-}H_1\cdots N_1$	0.82	1.92	2.650(3)	147.2
$C_{10}{-}H_{10}\cdots O_{2i}$	0.93	2.48	3.335(3)	153.0
$C_{18}{-}H_{18}\cdots O_{2i}$	0.93	2.50	3.351(5)	152.4

Symmetry code (i): $-x + 1/2, -y + 1, z + 1/2$.

were slightly larger than those of the other atoms. The displacement parameters of H atoms were fixed at $1.2U_{eq}$ of their parent carbon atom for aromatic groups, $1.5U_{eq}$ of their parent atoms for methyl and hydroxyl groups (Fig. 7).

On top of all this, it was seen that the imino groups adopt a (Z) configuration, with the bond lengths $C_{10}{-}N_1 = 1.282(3)$ Å, $N_1{-}N_2 = 1.398(3)$ Å, $C_6{-}N_2 = 1.296(3)$ Å (Table 3). These data show that there is significant elongation of the $N_1{-}N_2$ bond and contraction of the $C_6{-}N_2$ bond in comparison with thiazole group [51].

The dihedral angles between the rings formed through intramolecular hydrogen bond, $H_1{-}O_1$ and $C_{12}{-}C_{17}$ rings, $H_1{-}O_1$ and $S_1{-}C_6$ rings are 0,5(1) ° and 2,54(8)° respectively. It means that the whole molecule is almost planar except ethyl group. A significant intramolecular hydrogen bond occurs between the hydrazo atom and hydroxyl group of phenly systems, namely $O_1{-}H_1\ldots N_1$ [graph set S(6)] [52]. There are also two intermolecular hydrogen bonds. Hence as shown in hydrogen figure, pair molecules linked through the $C_{10}{-}H_{10}\ldots O_2$ (symmetry code: $-x + 1/2, -y + 1, z + 1/2$) and $C_{18}{-}H_{18}\ldots O_2$ (symmetry code: $-x + 1/2, -y + 1, z + 1/2$) hydrogen bonds, form an $R_2^1(6)$[52], The details of hydrogen bond are shown in Table 4.

5. Conclusions

In this paper, we have reported on the preparation of a new type of phthalonitrile derivative. This compound is used as a base for the preparation of a novel mononuclear metal-free phthalocyanine and six different metallophthalocyanines (Cu, Co, Ni, Zn, Pb and Mn). The preparations of the new products are supported by elemental analysis, IR, UV–vis, $^1H/^{13}C$ NMR, $^1H{-}^1H$ COSY, Mass spactra and DTA/TG measurements. As can be discussed (for DTA/TG experiments) from the result section, especially, in thermal motion of phthalocyanines, Metal-free, Cu, Co, Ni, Zn and Mn phthalocyanines show a good thermal stability whereas Pb phthalocyanine degrades the most rapidly. In the phthalocyanines, the thermal stabilities of CuPc, CoPc, NiPc and PbPc are lower than those of metal-free, ZnPc and MnPc derivatives.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2009.07.001.

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