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Synthesis of Carbocycles with the Fragments of Phenylenediamines and Their Copper(II), Cobalt(II), and Zinc(II) Complexes

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Abstract—Indandione reacts with *m*-phenylenediaminosulfonic acid or 2,4-diaminophenol to form compounds with phenylenediamine fragment. Complexes of these compounds with copper, cobalt, and zinc were synthesized. IR and UV spectroscopic data are presenred.

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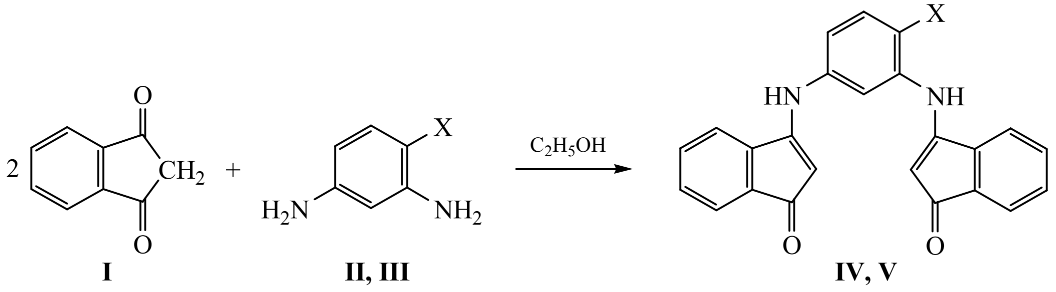
Among the variety of organic substances a great interest present high molecular compounds which have cyclic structure and contain not less than twelve atoms in the large inner cycle (nitrogen, carbon, metal atoms, etc.). They are called macrocyclic compounds.

Compounds of such type exhibit unique properties and are used in science, technique, and medicine as the pigments and dyes, thermo- and light stabilizers, organic semiconductors and catalysts of redox processes, medicinal remedies and biologically active compounds [1–7].

The work presented is the continuation of studies in the field of synthesis and investigation of physicochemical properties of macroheterocyclic compounds and their metal complexes of different structure [8–12].

On the basis of indandione **I** [13] and substituted *m*-phenylenediamines such as *m*-phenylenediaminesulfonic acid **II** and 2,4-diaminophenol **III** phenylenediamines **IV, V** were synthesized macrocycles according to the following scheme.



I **II, III** **IV, V**

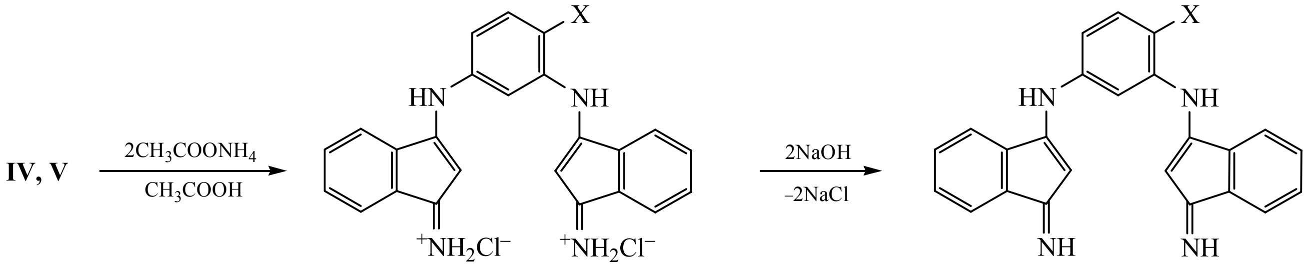
X = SO_3H (**II, IV**), OH (**III, V**).

Formation of arylenediamines **IV, V** proceeds in boiling ethanol for 8 h. Arylenediamines **IV, V** are powderlike dark green substances decomposing without melting and dissolving in DMF, DMSO, acetone, 1% sodium hydroxide solution, chloroform, and sulfuric acid. They do not hydrolyze in boiling HCl.

In the IR spectra of these substances absorption bands in the range 1725–1610 cm^{-1} corresponding to the carbonyl group bond vibrations, and also the band at 987 cm^{-1} related to S=O bond vibrations (compound **IV**) and a band at 2912 cm^{-1} belonging to the hydroxyl group bond vibrations (compound **V**) [14] were observed. Hence, IR spectra confirm the presence of these fragments and groups in the diamine molecules.

Electron absorption spectra of arylenediamines **IV, V** contain absorption bands in the range 250–800 nm.

Absorption in the range 350–390 nm (Fig. 1) relates to the electron transfers with the participation of indandione fragments. In the range of 500–600 nm the absorption is caused by the π–π-electron transfers in the conjugation chain of arylenediamine. The bands at 700–800 nm may be characteristic of the electron transfers in the arylenediamine molecules with intramolecular hydrogen bond. Amination of compounds **IV, V** was carried out with ammonium acetate in glacial acetic acid on boil. Addition of concentrated HCl to the solution obtained caused the precipitation of less soluble salts of arylenediamines hydrochlorides **VI, VII**. By treating their ethanolic solutions with alkali the carbocycles **VIII, IX** were obtained.



VI, VII **VIII, IX**

X = SO_3H (**VI, VIII**), OH (**VII, IX**).

Dihydrochlorides **VI, VII** are powders of black or grayish green coloration. Carbocycles **VIII, IX** have dark and yellowish green coloration respectively. In the IR spectra of dihydrochlorides **VI, VII** the absorption bands at 3563–2918 cm^{-1} corresponding to the NH_2 bond vibrations are observed. The band of azomethine group bond vibrations $\nu_{C=N}$ in the obtained carbocycles **VIII, IX** is located at 1475–1618 cm^{-1}.

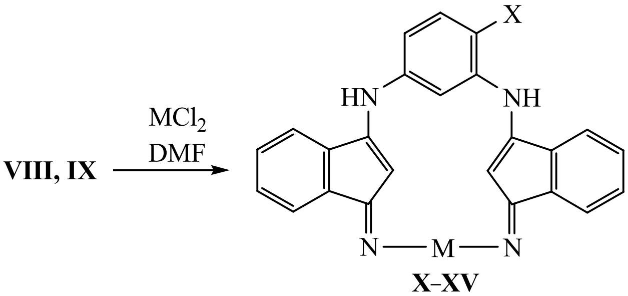
The carbocycles **VIII, IX** are characterized only by two absorption bands at 300–400 and 550–600 nm (Fig. 2).

Coordination of carbocycles with metal ions leads to significant and regular alteration in their physicochemical properties. The reason of it are the effects of coordination which appear in cyclic ligands due to redistribution of electrons on loosening the π-orbitals of ligands in the course of coordination.

The main way of obtaining metal complexes of macroheterocycles is heating them with metal salts (acetates, halides) in organic solvents such as pyridine, nitrobenzene, DMF [15–17]. But there exists also a template method of obtaining of metal complexes from diiminoisoindolines and diamines in the presence of metal salts [18]. Metallomacroheterocycles are less soluble in organic solvents as compared to corresponding macroheterocyclic ligands.

The researchers [19, 20] noted that some arylenes form metal complexes of the 1:1 and 1:2 composition with the transition metals. Formation of arylene complexes of the 1:1 composition on the basis of indanedione is also known [21].

Synthesis of metal complexes was carried out by the reaction of copper, cobalt, and zinc chlorides with the compounds **VIII, IX** in DMF on boil. Obtained complexes **X–XV** are powders having green coloration.



X–XV

X = SO_3H, OH; M = Cu^{2+}, Co^{2+}, Zn^{2+}.

Only terminal imino groups of compounds **VII, IX** take part in the reaction with metal ions that leads to formation of complexes of the 1:1 composition.

Structure of metal complexes **X–XV** was confirmed by the IR and electron spectroscopy, and their

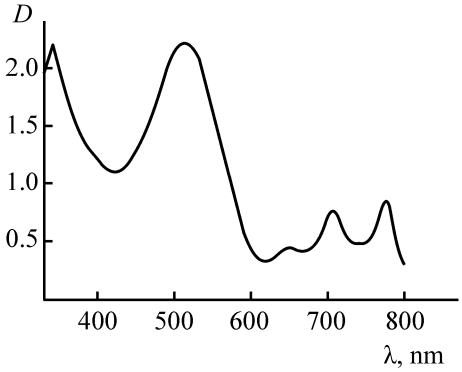


Fig. 1. Electron absorption spectrum of compound **IV** in DMF.

composition by the elemental analysis data. IR spectra of metal complexes are similar to the IR spectra of compounds **VIII**, **IX**, but they contain a series of absorption bands in the range 485–470 cm^{-1} characteristic of the N–M bond vibrations.

Electron absorption spectra of metal complexes **X–XV** are characterized by the absorption band in the range 300–900 nm (Fig. 3).

Presence of absorption bands in the range 800–900 nm in the sulfuric and acetic acids solutions tells about the presence of metal ions in these compounds.

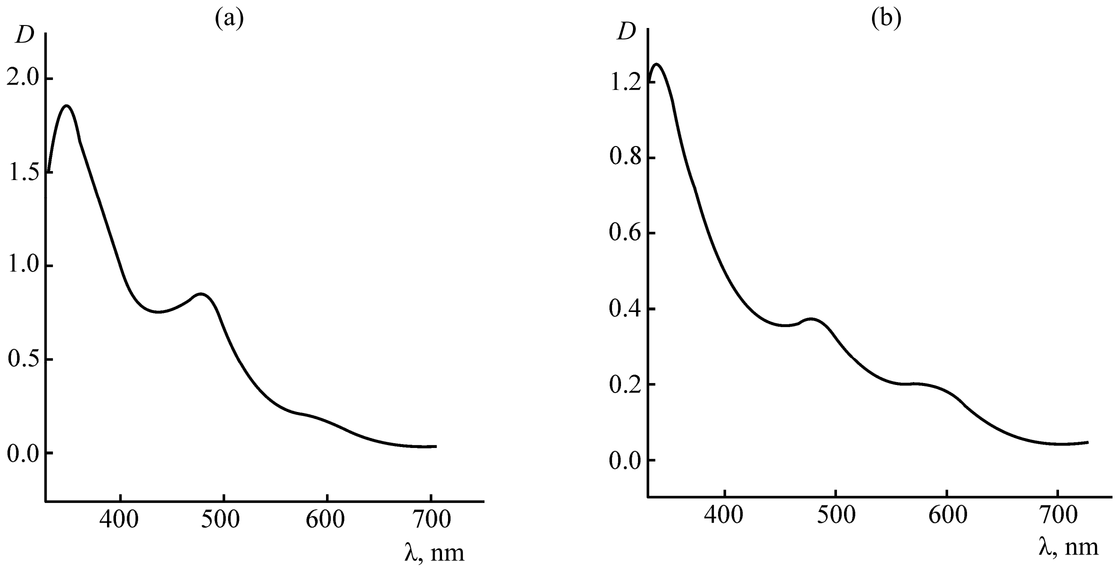


Fig. 2. Electron absorption spectra in DMF: (a) compound **VIII** and (b) compound **IX**.

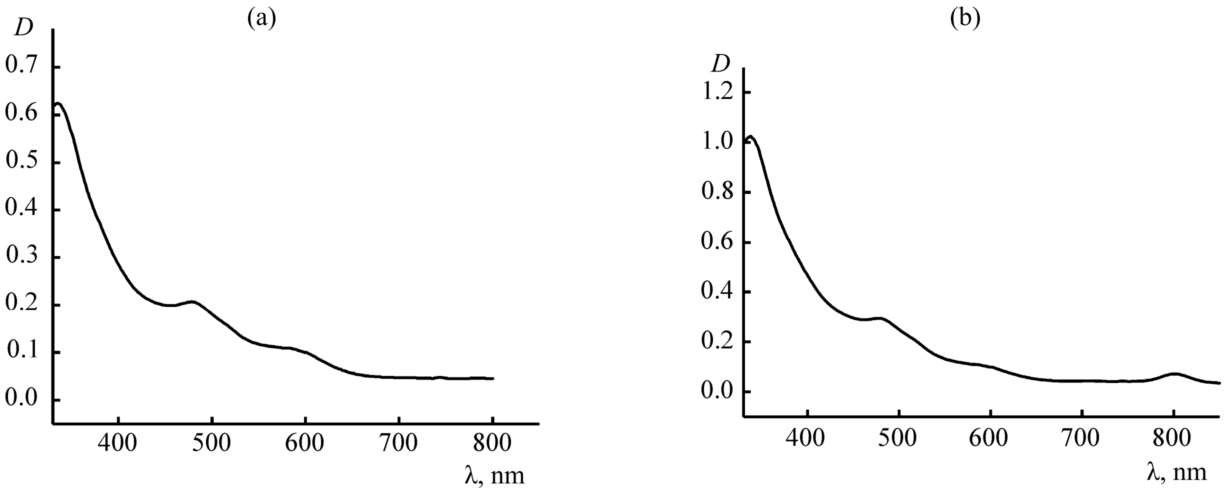


Fig. 3. Electron absorption spectrum in conc. H_2SO_4: (a) compound **X** and (b) compound **XIII**.

EXPERIMENTAL

Electron absorption spectra were measured on a Hitachi U-2010 spectrophotometer in the organic solvents, in the 1% NaOH solution, and in the concentrated H_2SO_4 in quartz cuvettes at 20°C. IR spectra were obtained on an Avatar 360 FT–IR ESP device in KBr. For the control of purity of the reaction products TLC on Silufol UV-254 plates was used, elution with 1:1 vol/vol acetone–chloroform.

1,3-Bis(3-oxoinden-1-yl)phenylenediaminosulfonic acid (IV). A mixture of 2.4 mmol of compound **I** and 1.2 mmol of *m*-phenylenediaminosulfonic acid **II** was heated in 15 ml of ethanol for 8 h under reflux. The precipitate formed was filtered off, washed with ethanol, and dried in air. Organic admixtures were removed by extraction in the Soxhlet apparatus with boiling acetone. Yield 0.35 g (66%), yellowish green crystalline substance, R_f 0.6, does not melt below 300°C. This compound is soluble in sulfuric acid, DMF, and 1% solution of sodium hydroxide. The product does not hydrolyze in boiling conc. HCl. IR spectrum, ν, cm^{-1}: (N–H) 3418; (O–H) 2891; (C=O) 1714; (C=C) 1687; δ(N–H) 1609; δ(C–H) 1349; δ(O–H) 1249; (C–N) 1221; (C–C) 1156; (S=O) 987; (C–S) 637. UV spectrum, λ_{max}, nm: in DMF 344, 515, 706, 775; in conc. H_2SO_4 332, 405; in 1% NaOH 328, 522. Found, %: C 64.1; H 3.3; N 5.9; O 17.4; S 6.8. $C_{24}H_{14}N_2O_3S$. Calculated, %: C 64.9; H 3.6; N 6.3; O 18.0; S 7.2.

Compound **V** was obtained analogously.

***N,N'*-(4-Hydroxyphenyl-1,3-diyldiamino)bis(3-aminoinden-1-one) (V)**. Yield 0.5 g (77%), crystalline green substance, R_f 0.5, does not melt below 300°C, soluble in sulfuric acid, in DMF, acetone, ethanol, chloroform, 1% NaOH solution. The product does not hydrolyze with boiling concentrated HCl. IR spectrum, ν, cm^{-1}: (N–H) 3408; (O–H) 2912; (C=O) 1733; (C=C) 1686; δ(N–H) 1462; δ(C–H) 1350; (C–C) 1272; δ(O–H) 1247; (C–O) 1220; (C–N) 1203. UV spectrum, λ_{max}, nm: in DMF 512, 645, 706, 775; in conc. H_2SO_4 338, 390, 505; in ethanol 338, 523, 710, 782; in chloroform 372, 393, 577; in 1% NaOH solution 362, 521. Found, %: C 73.9; H 3.8; N 7.2; O 12.2. $C_{24}H_{14}\cdot N_2O_3$. Calculated, %: c 75.8; H 4.2, N 7.4; O 12.6.

1,2-Bis(3-iminoinden-1-yl)phenylenediaminosulfonic acid dihydrochloride (VI). A mixture of 0.8 mmol of compound **I** and 26 mmol of ammonium acetate was refluxed in 10 ml of glacial acetic acid for 2 h. After that the reaction mixture was cooled, diluted with 10 ml of water, treated with 5 ml of hydroghloric acid and kept for 3 h at room temperature. The precipitate formed was filtered off and dried in air. Yield 0.11 g (32%), black crystalline substance, R_f 0.55. IR spectrum, ν, cm^{-1}: (N–H_2) 3408; (O–H) 2912; (C=C) 1686; δ(C–H) 1350; (C–C) 1272; δ(O–H) 1247; (C–N) 1203; (S=O) 980; (C-S) 637. UV spectrum, λ_{max}, nm: in DMF 354. Found, %: C 59.8; H 3.9; N 11.3; O 10.0; S 6.5. $C_{24}H_{29}N_4O_3SCl_2$. Calculated, %: C 60.0; H 4.2; N 11.7; O 10.0; S 6.7.

Compound **VII** was obtained analogously.

4(-4-Hydroxyphenyl-1,3-diyldiamino)bis(inden-1-imine) hydrochloride (VII). Yield 0.27 g (54%), greyish green crystals, R_f 0.45. IR spectrum, ν, cm^{-1}: (N–H_2) 3408; (O–H) 2912; (C=C) 1686; δ(C–H) 1350; (C–C) 1272; δ(O–H) 1247); (C–O) 1220; (C–N) 1203. UV spectrum, λ_{max}, nm: in DMF 341, 425, 485; in chloroform 341, 425, 485; in concentrated H_2SO_4 340, 475. Found, %: C 63.6; H 4.3; N 12.0, O 3.4. $C_{24}H_{20}N_4\cdot OCl_2$. Calculated, %: C 63.9; H 4.4; N 12.4; O 3.6.

1,3-Bis(3-iminoinden-1-yl)phenylenediaminosulfonic acid (VIII). Compound **VI** was dissolved in the least possible volume of ethanol under heating and neutralized with 10% NaOH solution. The mixture obtained was kept for 24 h, and compound **VIII** was filtered off and washed with small amount of 1:1 aqueous ethanol. Yield 0.06 g (50%), crystalline dark green substance, decomposition point 265°C, R_f 0.65. IR spectrum, ν, cm^{-1}: NH 3454; (O–H) 2912; (C–N) 1611; (C=C) 1605; δ(N–H) 1462; δ(C–H) 1350; (C–C) 1272; δ(O–H) 1247; (S=O) 1088; (C-S) 976. UV spectrum, λ_{max}, nm: in DMF 330, 585; in chloroform 335, 420, 480; in concentrated H_2SO_4 349, 480.Found, %: C 65.1; H 4.1; N 12.1; O 19.4; S 7.1. $C_{24}H_{18}N_4O_3S$. Calculated, %: C 65.2; H 4.1; N 12.7; O 10.9; S 7.1.

Compound **IX** was obtained analogously.

4-(4-Hydroxyphenyl-1,3-diyldiamino)bis(inden-1-imine) (IX). Yield 0.22 g (63%), yellowish green crystals, R_f 0.6, decomposition point 243°C. IR spectrum, ν, cm^{-1}: (N–H) 3408; (O–H) 2912; (C=C) 1686; δ(N–H) 1462; δ(C–H) 1350; (C–C) 1272; δ(O–H) 1247; (C–O) 1220; (C–N) 1203. UV spectrum, λ_{max}, nm: in DMF 335, 480; in concentrated H_2SO_4 341, 595; in chloroform 335, 480. Found, %: C 75.8; H 4.5; N 14.7; O 4.0. $C_{24}H_{18}N_4O$. Calculated, %: C 76.2; H 4.8; N 14.8; O 4.2.

Metal complex X. A mixture of 0.79 mmol of compound **VIII** and 1.5 mmol of copper chloride was refluxed in DMF for 4 h. After the reaction was complete the mixture obtained was cooled and poured in 10 ml of water. The precipitate formed was filtered off, washed with water until the absence of chloride ions (test with silver nitrate) and dried at 150°C. Yield 0.033 g (84%), yellowish green crystalline substance does not melting up to 300°C. Soluble in chloroform, DMF, sulfuric and acetic acids. IR spectrum, ν, cm^{-1}: (N–H) 3480; (OH) 3054; (C=N) 1712; (C=C) 1611; (C–N) 1576); (C–C) 1203; (S=O) 1003; (C-S) 654; (N–M) 475. UV spectrum, λ_{max}, nm: in DMF 341, 408, 603; in concentrated H_2SO_4 300, 584, 603, 744; in chloroform 583, 604, 743, in acetic acid 335, 479, 744, 789. Found, %: C 56.9; H 3.0; N 10.2; O 9.3; S 6.0; Cu^{2+} 14.2. $C_{24}H_{16}N_4O_3SCu$. Calculated, %: C 57.9; H 3.2; N 11.1; O 9.5; S 6.4; Cu^{2+} 14.6.

Compounds **XI–XV** were obtained analogously.

Metal complex XI. Yield 0.035 g (85%), green crystals do not melting up to 300^{o}C, soluble in chloroform, DMF, in the sulfuric and acetic acids IR spectrum, ν, cm^{-1}: (N–H) 3470; (C–H) 3416; (O–H) 2924; (C=N) 1712; (C=C) 1611; (C–N) 1353; (C–C) 1203; (S=O) 1004; (C–S) 654; (N–M) 485. UV spectrum, λ_{max}, nm: in concentrated H_2SO_4 320, 478, 743; in chloroform 300. 460, 744; in acetic acid 743, 800; in DMF 301, 400, 582; 745. Found, %: C 57.3; H 3.0; N 10.9; O 9.5; S 6.4; Co^{2+} 11.2. $C_{26}H_{16}N_4O_3SCo$. Calculated, %: C 57.7; H 3.2; N 11.2; O 9.6; S 6.4; Co^{2+} 11.8.

Metal complex XII. Yield 0.034 (84%), dark green crystals does not melting up to 300^{o}C, soluble in chloroform, DMF, in the sulfuric and acetic acids. IR spectrum, ν, cm^{-1}: (C–H) 3554; (N–H) 3419; (O–H) 3070; (C=N) 1712; (C=C) 1611; (C–N) 1355; (C–C) 1203; (S=O) 1003; (C-S) 654; (N–M) 482. UV spectrum, λ_{max}, nm: in concentrated H_2SO_4 338, 478, 600, 744, 801; in chloroform 310, 480, 744, 845; in acetic acid 584, 603, 743. Found, %: C 56.1; H 3.0; N 11.0; O 9.0; S 6.1; Zn^{2+} 12.5. $C_{24}H_{16}N_4O_2SZn$. Calculated, %: C 57.0; H 3.1; N 11.1; O 9.5; S 6.3; Zn^{2+} 13.0.

Metal complex XIII. Yield 0.038 g (88%), yellowish green crystals does not melting up to 300°C soluble in chloroform, DMF, in the sulfuric and acetic acids.

IR spectrum, ν, cm^{-1}: (C–H) 3417; (N–H) 3416; (O–H) 3229; (C=N) 1712; (C=C) 1611; (C–N) 1354; (C=C) 1203; (N–M) 480. UV spectrum, λ_{max}, nm: in DMF 470, 586, 743; in concentrated H_2SO_4 335, 478, 743; in chloroform 305, 586, 744; in acetic acid 300, 583, 743, 880. Found, %: C 65.1; H 3.2; N 12.9; O 3.6; Cu^{2+} 14.2. $C^{24}H_{16}N_4OCu$. Calculated, %: C 65.5; H 3.6; N 12.7; O 3.6; Cu^{2+} 14.4.

Metal complex XIV. Yield 0.03 g (79%), light green crystals do not melting up to 300°C, soluble in chloroform, DMF, in the sulfuric and acetic acids. IR spectrum, ν, cm^{-1}: (C–H) 3546; (N–H) 3413; (O–H) 3229; (C–N) 1712; (C=C) 1613; (C–N) 1353; (C–C) 1203; (N–M) 470. UV spectrum, λ_{max}, nm: in concentrated H_2SO_4 332, 476, 582, 743; in chloroform 490, 743, 778, 882; in DMF 480, 744, 898.Found, %: C 65.9; H 3.4; N 12.0; O 3.7; Co^{2+} 13.1. $C_{26}H_{16}N^3OCo$. Calculated, %: C 55.1; H 3.6; N 12.8; O 3.7; Co^{2+} 13.5.

Metal complex XV. Yield 0.027 g (80%), dark green crystals do not melting up to 300°C, soluble in chloroform, DMF, in the sulfuric and acetic acids. IR spectrum, ν, cm^{-1}: (C–H) 3540; (N–H) 3415; (O–H) 3223; (C=N) 1713; (C=C) 1615; (C–N) 1352; (C–C) 1203; (N–M) 479. UV spectrum, λ_{max}, nm: in concentrated H_2SO_4 330, 478, 583, 743; in chloroform 310, 490, 743, 882; in acetic acid 300. 385, 586, 743, 900; in DMF 380, 490, 743, 898. Found, %: C 65.0; H 3.6; N 12.0; O 3.6; Zn^{2+} 14.6. $C_{24}H_{16}N_4OZn$. Calculated, %: C 65.25; H 3.65; N 12.68; O 3.67; Zn^{2+} 14.8.

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