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The use of metal chelators in the synthesis of monomethine cyanine dyes

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Abstract

A series of monomethine cyanine dyes incorporating a transient divalent metal complex have been synthesized and characterized with elemental analyses, visible absorption, IR, ^{1}H NMR and mass spectroscopy. The correlations between the structure and properties of these dyes have been studied. This work presents stabilized monomethine cyanine metal complex dyes that exhibit an enhanced resistance to light, heat and moisture, in comparison with non-stabilized cyanine dyes. They are, thus, of potential interest for use in optical recording media.

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1. Introduction

There is ongoing interest in the use of cyanine dyes for storage disk laser system [1–3]. Cyanine dyes have become popular in photographic applications, where the dyes adsorbed on silver halide act as sensitizers [4,5]. Cyanine dyes are cheap, easy to synthesize, and show very good optical properties [6–10], but their stability is not good. Therefore, it is of value to study and solve the photostability problem of cyanine dyes to make them suitable for high density optical recording and storage. Addition of transient metal chelate compounds as quenchers in the synthesis of cyanine dyes enhances their photostability, and essentially inhibits their decolorization by light [11–13].

This paper reports the synthesis and characterization of a series of new stabilized monomethine cyanine metal complex dyes, and also their structure–property relationships of these dyes from their visible absorption spectra.

2. Experimental

Melting points were recorded on a Galenkanp melting point apparatus and are uncorrected. Microanalyses were carried out at the Microanalytical center at Cairo University. Infrared spectra were recorded in potassium bromide on a Perkin–Elmer 127B Infrared spectrophotometer. ^{1}H NMR spectra were recorded in deuterated DMSO-d_6 on a Varian Gemini 200 NMR spectrometer using tetramethylsilane as an internal reference. Mass spectra were recorded on HpMs 6988 spectrometer and electron-impact (EI). Visible spectra (300–700 nm) were recorded on a Shimadzu UV/visible 160-A spectrophotometer at the Aswan Faculty of Science. All reagents and solvents were obtained from Aldrich Chemical Company (Milwaukee, WI, USA).

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Synthesis of 4-formyl-3methyl-1-phenyl pyrazol-5-one (**1**) was carried out according to Ref. [14].

*2.1. Synthesis of 3-methyl-6-metalo-1-phenylpyrazolo-5,7-dioxo-heterocyclic metal complex ylide chloride (**2a–c**)*

A mixture of compound **1** (2.02 g, 0.01 mol) and metal divalent chloride ($NiCl_2$, $CoCl_2$, and $CuCl_2$) (0.01 mol) was dissolved in absolute ethanol (30 ml) and piperidine (3 ml) was added. The reaction mixture was heated on a water-bath with stirring for 1 h. The solvent was evaporated, cooled and the precipitated solid was filtered off and washed with ether to give compounds **2a–c**.

(**2a**): Yield 83%; m.p. 175–177 °C, Anal. cald for $C_{11}H_9N_2O_2ClNi$ (295.19): C, 44.72; H, 3.05; N, 9.48. Found: C, 44.55; H, 2.91; N, 9.63. Ms: $m/z = 297$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1510 cm^{-1} (C=N), 1580 cm^{-1} (C=C) and 1690 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.15 ppm (s, 3H, CH_3-pyrazole), 7.10–7.95 ppm (m, 5H, Ar-H), 10.52 ppm (s, 1H, CH).

(**2b**): Yield 79%; m.p. 183–185 °C, Anal. cald for $C_{11}H_9N_2O_2ClCo$ (295.44): C, 44.68; H, 3.05; N, 9.48. Found: C, 44.73; H, 3.15; N, 9.57. Ms: $m/z = 297$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1695 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.15 ppm (s, 3H, CH_3-pyrazole), 7.10–7.95 ppm (m, 5H, Ar-H), 10.52 ppm (s, 1H, CH).

(**2c**) Yield 67%; m.p. 145–147 °C, Anal. cald for $C_{11}H_9N_2O_2ClCu$ (300.04): C, 43.99; H, 3.00; N, 9.33. Found: C, 44.15; H, 3.11; N, 9.47. Ms: $m/z = 302$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1510 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1690 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.12 ppm (s, 3H, CH_3-pyrazole), 7.15–7.95 ppm (m, 5H, Ar-H), 10.42 ppm (s, 1H, CH).

*2.2. Synthesis of 3-methyl-6-metalo-1-phenylpyrazolo-5,7-dioxo-heterocyclic metal complex ylide chloride-4[2(4)]-monomethine cyanine dyes (**3a–e**)*

A mixture of compounds **2a–c** (0.01 mol) and 2(4)-methyl substituted heterocyclic quaternary salts ((1,2-dimethylpyridinium, 1,2-dimethylquinolinium and 1,4-dimethylpyridinium) iodides) (0.01 mol) was dissolved in absolute ethanol (20 ml) and piperidine (3 ml) was added. The reaction mixture was refluxed for 12 h, filtered hot, concentrated and cooled. The precipitated products were filtered off and dried and then recrystallized from methanol to give compounds **3a–e**.

(**3a**) Yield 55%; m.p. 217–219 °C, Anal. cald for $C_{18}H_{16}N_3O_2ClNi$ (400.19): C, 53.97; H, 4.00; N, 10.50. Found: C, 54.13; H, 3.85; N, 10.39. Ms: $m/z = 402$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1510 cm^{-1} (C=N), 1580 cm^{-1} (C=C), 2980 cm^{-1} (CH_3–N^+I) and 1693 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.20 ppm (s, 3H, CH_3-pyrazole), 1.50 ppm (s, 3H, CH3–), 6.55–8.15 ppm (m, 10H, Ar-H + het-H + CH=).

(**3b**) Yield 83%; m.p. 195–197 °C, Anal. cald for $C_{22}H_{18}N_3O_2ClNi$ (450.19): C, 58.64; H, 4.00; N, 9.33. Found: C, 58.73; H, 4.11; N, 9.41. Ms: $m/z = 452$. IR (ν^{KBr}, cm^{-1}): 515 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1585 cm^{-1} (C=C), 2980 cm^{-1} (CH_3–N^+I) and 1690 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.09 ppm (s, 3H, CH_3-pyrazole), 1.56 ppm (s, 3H, CH3–), 6.65–8.11 ppm (m, 12H, Ar-H + het-H + CH=).

(**3c**) Yield 61%; m.p. 225–227 °C, Anal. cald for $C_{18}H_{16}N_3O_2ClNi$ (400.19): C, 53.97; H, 4.00; N, 10.50. Found: C, 54.17; H, 4.15; N, 10.63. Ms: $m/z = 402$.

(**3d**) Yield 79%; m.p. 135–137 °C, Anal. cald for $C_{22}H_{18}N_3O_2ClCo$ (450.44): C, 58.61; H, 4.00; N, 9.32. Found: C, 58.87; H, 3.91; N, 9.47. Ms: $m/z = 452$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 2980 cm^{-1} (CH_3–N^+I) and 1695 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.11 ppm (s, 3H, CH_3-pyrazole), 1.50 ppm (s, 3H, CH3–), 6.70–8.15 ppm (m, 12H, Ar-H + het-H + CH=).

(**3e**) Yield 75%; m.p. 187–189 °C, Anal. cald for $C_{22}H_{18}N_3O_2ClCu$ (455.04): C, 58.02; H, 3.96; N, 9.23. Found: C, 57.93; H, 4.09; N, 9.35. Ms: $m/z = 457$.

*2.3. Synthesis of 3-methyl-6-imino-1-phenyl-pyrano[2,3-c]pyrazole-5-carboxyamide/carboxylate compounds (**4a–c**)*

Synthesis of **4a–c** was carried out according to Ref. [15].

*2.4. Synthesis of 3-methyl-7-metalo-1-phenylpyrazol[2,3-c]pyrano[3,4-b]oxazine-ylide chloride compounds (**5a–d**)*

Using a mixture of compounds **4a**,**b** (0.01 mol) and metal dichloride (0.01 mol), the products were obtained essentially using the same method as for compounds **2a–c** to give compounds **5a–d**.

(**5a**) Yield 85%; m.p. 155–157 °C, Anal. cald for $C_{16}H_{14}N_3O_3ClCu$ (395.04): C, 48.62; H, 3.54; N, 10.63. Found: C, 48.49; H, 3.63; N, 10.51. Ms: $m/z = 396$. IR (ν^{KBr}, cm^{-1}): 522 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1695 cm^{-1} (C=O). ^1H NMR (DMSO, 200 MHz) 1.12 ppm (s, 3H, CH_3-pyrazole), 2.15 ppm (t, 3H, CH_3–), 2.65 ppm (q, 2H, CH_2–), 6.55–7.95 ppm (m, 6H, Ar-H + het-H).

(**5b**) Yield 73%; m.p. 147–149 °C, Anal. cald for $C_{14}H_{11}N_4O_2ClNi$ (361.19): C, 46.52; H, 3.05; N, 15.50. Found: C, 46.41; H, 3.11; N, 15.43. Ms: *m*/*z* = 362. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1690 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.15 ppm (s, 3H, CH_3-pyrazole), 4.55 ppm (s, 2H, NH_2–), 6.72–7.95 ppm (m, 6H, Ar-H + het-H).

(**5c**) Yield 77%; m.p. 165–167 °C, Anal. cald for $C_{14}H_{11}N_4O_2ClCo$ (361.44): C, 46.48; H, 3.04; N, 15.49. Found: C, 46.61; H, 3.15; N, 15.59. Ms: *m*/*z* = 363.

(**5d**) Yield 67%; m.p. 133–135 °C, Anal. cald for $C_{14}H_{11}N_4O_2ClCu$ (366.04): C, 45.90; H, 3.01; N, 15.30. Found: C, 46.07; H, 2.91; N, 15.41. Ms: *m*/*z* = 368.

*2.5. Synthesis of 3-methyl-7-metalo-1-phenylpyrazolo[2,3-c]pyrano[3,4-b]oxazine-ylide chloride compounds-5[2(4)]-monomethine cyanine dyes (**6a–e**)*

Using a mixture of compounds **5a–d** (0.01 mol) and 2(4)-methyl substituted heterocyclic quaternary salts ((1,2-dimethylpyridinium, 1,2-dimethylquinolinium and 1,4-dimethylpyridinium) iodides) (0.01 mol), the products were obtained essentially using the same method as for compounds **3a–e** to give compounds **6a–e**.

(**6a**) Yield 87%; m.p. 176–178 °C, Anal. cald for $C_{25}H_{19}N_4O_2ClCu$ (506.04): C, 59.28; H, 3.76; N, 11.07. Found: C, 59.49; H, 3.65; N, 10.91. Ms: *m*/*z* = 501. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1690 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.12 ppm (s, 3H, CH_3-pyrazole), 1.56 ppm (s, 3H, CH_3–), 6.50–8.15 ppm (m, 13H, Ar-H + het-H + CH=).

(**6b**) Yield 63%; m.p. 166–168 °C, Anal. cald for $C_{21}H_{17}N_4O_2ClNi$ (451.19): C, 55.85; H, 3.77; N, 12.41. Found: C, 55.49; H, 3.65; N, 12.51. Ms: m/z = 452. IR (ν^{KBr}, cm^{-1}): 523 cm^{-1} (M–O), 1510 cm^{-1} (C=N), 1585 cm^{-1} (C=C) and 1695 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.11 ppm (s, 3H, CH_3-pyrazole), 1.55 ppm (s, 3H, CH_3–), 6.650–8.12 ppm (m, 11H, Ar-H + het-H + CH=).

(**6c**) Yield 87%; m.p. 176–178 °C, Anal. cald for $C_{25}H_{19}N_4O_2ClNi$ (501.19): C, 59.86; H, 3.79; N, 11.17. Found: C, 59.77; H, 3.87; N, 11.41. Ms: *m*/*z* = 502. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 1580 cm^{-1} (C=C) and 1690 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.12 ppm (s, 3H, CH_3-pyrazole), 1.55 ppm (s, 3H, CH_3–), 6.57–8.12 ppm (m, 13H, Ar-H + het-H + CH=).

(**6d**) Yield 65%; m.p. 147–149 °C, Anal. cald for $C_{21}H_{17}N_4O_2ClNi$ (451.19): C, 55.85; H, 3.77; N, 12.41. Found: C, 55.76; H, 3.53; N, 12.61. Ms: *m*/*z* = 453.

(**6e**) Yield 83%; m.p. 185–187 °C, Anal. cald for $C_{25}H_{19}N_4O_2ClCo$ (501.44): C, 59.83; H, 3.79; N, 11.17. Found: C, 59.73; H, 3.63; N, 11.33. Ms: *m*/*z* = 503.

2.6. Synthesis of 5-acetyl-3-methyl-6-oxo-1-phenylpyrazolo[4,5-b]pyridine (7)

A mixture of compound **4c** (3.25 g, 0.01 mol) and ammonium acetate (1.54 g, 0.02 mol) was refluxed in acetic acid (20 ml) for 3 h. The mixture was concentrated, cooled and the precipitated solid was collected, washed with methanol and recrystallized from ethanol to a give brownish red product, compound **7**.

(**7**) Yield 87%; m.p. 143–145 °C, Anal. cald for $C_{15}H_{13}N_3O_2$ (267): C, 67.42; H, 4.87; N, 15.73. Found: C, 67.59; H, 4.65; N, 15.91. Ms: *m*/*z* = 268. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1520 cm^{-1} (C=N), 3400 cm^{-1} (NH), 1670 cm^{-1} (C=O, CO–CH_3) and 1680 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.15 ppm (s, 3H, CH_3-pyrazole), 2.71 ppm (s, 3H, CH_3–C=O), 6.85–7.95 ppm (m, 6H, Ar-H + het-H), 9.75 ppm (s, 1H, NH).

*2.7. Synthesis of 3,5-dimethyl-1-phenylpyrazolo[4,5-b]pyridine-7-cobalto-heterocyclic ylide chloride (**8**)*

A mixture of compound **7** (2.67 g, 0.01 mol) and cobalt chloride was dissolved in absolute ethanol (30 ml) and piperidine (3 ml) was added. The reaction mixture was heated on water-bath with stirring for 1 h. The solvent was evaporated, cooled and the precipitated solid was filtered off and washed with ether to give compound **8**.

Yield 69%; m.p. 165–167 °C, Anal. cald for $C_{15}H_{12}N_3O_2ClCo$ (360.44): C, 49.94; H, 3.33; N, 11.65. Found: C, 49.75; H, 2.99; N, 11.43. Ms: *m*/*z* = 362. IR (ν^{KBr}, cm^{-1}): 515 cm^{-1} (M–O), 1510 cm^{-1} (C=N) and 1695 cm^{-1} (C=O). ^{1}H NMR (DMSO, 200 MHz) 1.17 ppm (s, 3H, CH_3-pyrazole), 2.52 ppm (s, 3H, CH_3), 6.71–8.11 ppm (m, 6H, Ar-H + het-H).

*2.8. Synthesis of 3-methyl-1-phenylpyrazolo[4,5-b]pyridine-7-cobalto-5[4(1)]-monomethine cyanine dyes (**9a–c**)*

A mixture of compound **8** (3.60 g, 0.01 mol) and 4(1)-heterocyclic quaternary salts ((pyridinium, quinolinium and isoquinolinium) methyl iodides) (0.01 mol) was dissolved in absolute ethanol (20 ml) and piperidine (3 ml) was added. The reaction mixture was refluxed for 12 h, filtered hot, concentrated and cooled. The precipitated solid was filtered off and dried. The products were recrystallized from methanol to give compounds **9a–c**.

(**9a**) Yield 59%; m.p. 167–169 °C, Anal. cald for $C_{21}H_{17}N_4O_2ICo$ (542.94): C, 46.41; H, 3.13; N, 10.31. Found: C, 46.23; H, 3.35; N, 10.29. Ms: $m/z = 545$. IR (ν^{KBr}, cm^{-1}): 520 cm^{-1} (M–O), 1510 cm^{-1} (C=N), 2940 cm^{-1} (CH_3–N^+I). ^{1}H NMR (DMSO, 200 MHz) 1.19 ppm (s, 3H, CH_3-pyrazole), 3.95 ppm (s, 3H, CH_3–N^+), 6.52–8.11 ppm (m, 11H, Ar-H + het-H + CH=).

(**9b**) Yield 79%; m.p. 211–213 °C, Anal. cald for $C_{25}H_{19}N_4O_2ICo$ (592.94): C, 50.60; H, 3.20; N, 9.45. Found: C, 50.85; H, 3.37; N, 9.35. Ms: $m/z = 595$. IR (ν^{KBr}, cm^{-1}): 5222 cm^{-1} (M–O), 1515 cm^{-1} (C=N), 2940 cm^{-1} (CH_3–N^+I). ^{1}H NMR (DMSO, 200 MHz) 1.15 ppm (s, 3H, CH_3-pyrazole), 3.93 ppm (s, 3H, CH_3–N^+), 6.65–8.13 ppm (m, 13H, Ar-H + het-H + CH=).

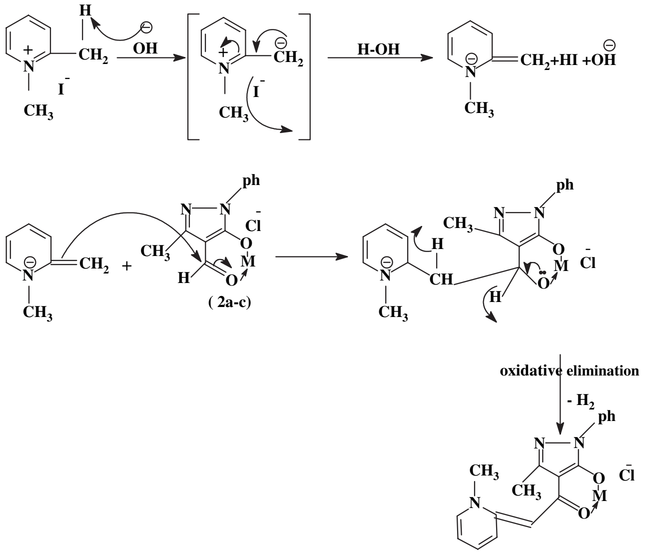
(**9c**) Yield 65%; m.p. 177–179 °C, Anal. cald for $C_{25}H_{19}N_4O_2ICo$ (592.94): C, 50.60; H, 3.20; N, 9.45. Found: C, 50.77; H, 3.13; N, 9.65. Ms: $m/z = 595$.

3. Results and discussion

3.1. Synthesis

Reaction of equimolar amounts of 4-formyl-3-methyl-1-phenylpyrazol-5-one (**1**) [14] with metal divalent chloride ($NiCl_2$, $CoCl_2$, and $CuCl_2$) in the presence of piperidine as a basic catalyst and ethanol as solvent produced the desired 3-methyl-6-metalo-1-phenylpyrazolo-5,7-dioxo-heterocyclic ylide chloride compounds (**2a–c**). The reaction of equimolar amounts of compounds (**2a–c**) with 2(4)-methyl substituted heterocyclic quaternary salts ((1,2-dimethylpyridinium, 1,2-dimethylquinoli-nium and 1,4-dimethylpyridinium) iodides) in the presence of piperidine as a basic catalyst and ethanol as solvent produced the corresponding 3-methyl-6-metalo-1-phenyl pyrazolo-5,7-dioxo-heterocyclic ylide chloride-4[2(4)]-monomethine cyanine dyes (**3a–e**, Scheme 1).

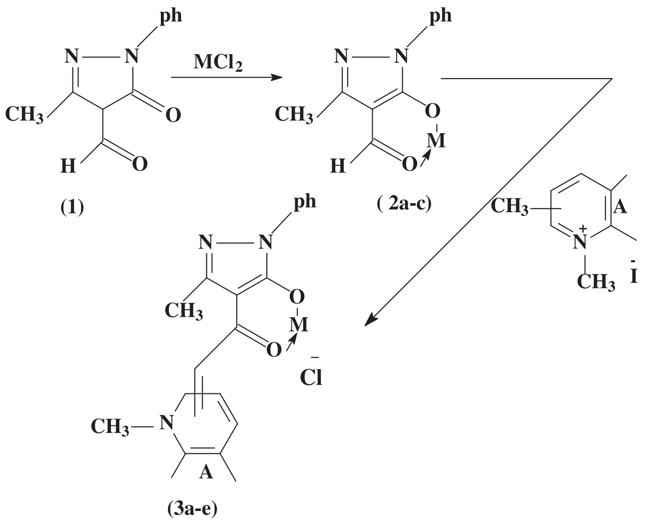
The formation of such dyes (**3a–e**) incorporating 3-methyl-6-metalo-1-phenylpyrazolo-5,7-dioxo-heterocyclic ylide chloride was suggested to proceed according to the relative stability of both reactants either compounds **2a–c** and/or 2(4)-methyl heterocyclic quaternary salts. Thus, the piperidine catalyst abstracts proton from 2(4)-methyl heterocyclic quaternary salts, resulting in the mesomeric stabilized anhydro base form (A). The latter form undergoes nucleophilic addition reaction of the 6-metalo-1-phenylpyrazolo-5,7-dioxo-heterocyclic ylide chloride resulting in adducts of formula (B) then followed by an oxidative elimination process to produce the desired dyes as follows:



The structure of compounds **2a–c** and **3a–e** was confirmed by analytical and spectral data. Infrared (IR) spectra of compounds **2a** and **3a** showed general absorption bands at 1510 cm^{-1} (νC=N), 1580 cm^{-1} (νC=C), 520 cm^{-1} (νM–O), and 1693 cm^{-1} (C=O) and 2980 cm^{-1} (νCH_3–N) for compound **3a**. ^{1}H NMR (DMSO) of compound **2a** showed signals at 1.15 ppm (s, 3H, CH_3-pyrazole), 7.10–7.95 ppm (m, 5H, Ar-H), 10.52 ppm (s, 1H, CH) and for compound **3a** reveals signals at 1.20 ppm (s, 3H, CH_3-pyrazole), 1.50 ppm (s, 3H, N–CH_3), 6.55–8.15 ppm (m, 10H, Ar-H + het-H + CH=).

Reaction of equimolar amounts of 6-imino-3-methyl-1-phenyl-pyrano[2,3-*c*]pyrazole-5-carboxyamide/carboxylate compounds (**4a**,**b**) [15] with transient divalent metal chloride in the presence of piperidine as a basic catalyst and ethanol as solvent produced the corresponding 3-methyl-7-metalo-1-phenylpyrazolo[2,3-*c*]pyrano[3,4-*b*]-oxazine-ylide chloride compounds (**5a–d**). The reaction of equimolar amounts of compounds **5a–d** with 2(4)-methyl substituted heterocyclic quaternary salts ((1,2-dimethylpyridinium, 1,2-dimethylquinolinium and 1,4-dimethylpyridinium) methiodides) in the presence of piperidine as a basic catalyst and ethanol as solvent produced the corresponding 3-methyl-7-metalo-1-phenylpyrazolo[2,3-*c*]pyrano[3,4-*b*]-oxazine-ylide chloride-5[2(4)]-monomethine cyanine dyes (**6a–e**, Scheme 2).

The structure of compounds **5a–d** and **6a–e** was confirmed by analytical and spectral data. Infrared (IR) spectra of compounds **5b** and **6a** showed general absorption bands at 1515 cm^{-1} (νC=N), 1585 cm^{-1} (νC=C), 520 cm^{-1} (νM–O), 2928 cm^{-1} and 2970 cm^{-1} (νCH_3I) and 1690 cm^{-1} (C=O) for compound **6a**. ^{1}H NMR (DMSO) of compound **5b** showed signals at



(2a-c):- a) M = Ni; b) M= Co; c) M = Cu

(3a-e):

a) M = Ni, A = 1-methylpyridin-2-ium ; b) M = Ni, A = 1-methylquinolin-2-ium;

c) M = Ni, A = 1-methylpyridin-4-ium; d) M = Co, A = 1-methylquinolin-2-ium;

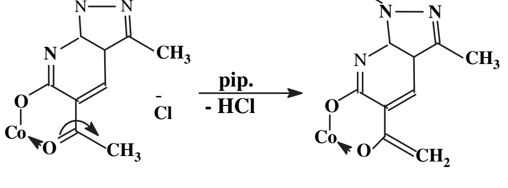
e) M = Cu, A = 1-methylquinolin-2-ium

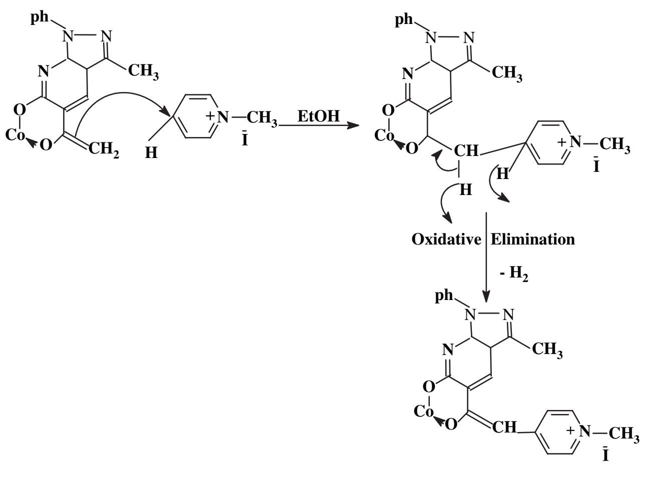
Scheme 1.

1.15 ppm (s, 3H, CH_3-pyrazole), 4.55 ppm (s, 2H, NH_2), 6.72–7.95 ppm (m, 6H, Ar-H + het-H), and for compound **6a** reveals signals at δ 1.12 ppm (s, 3H, CH_3-pyrazole), 1.56 ppm (s, 3H, N–CH_3), 6.50–8.15 ppm (m, 13H, Ar-H + het-H + CH=).

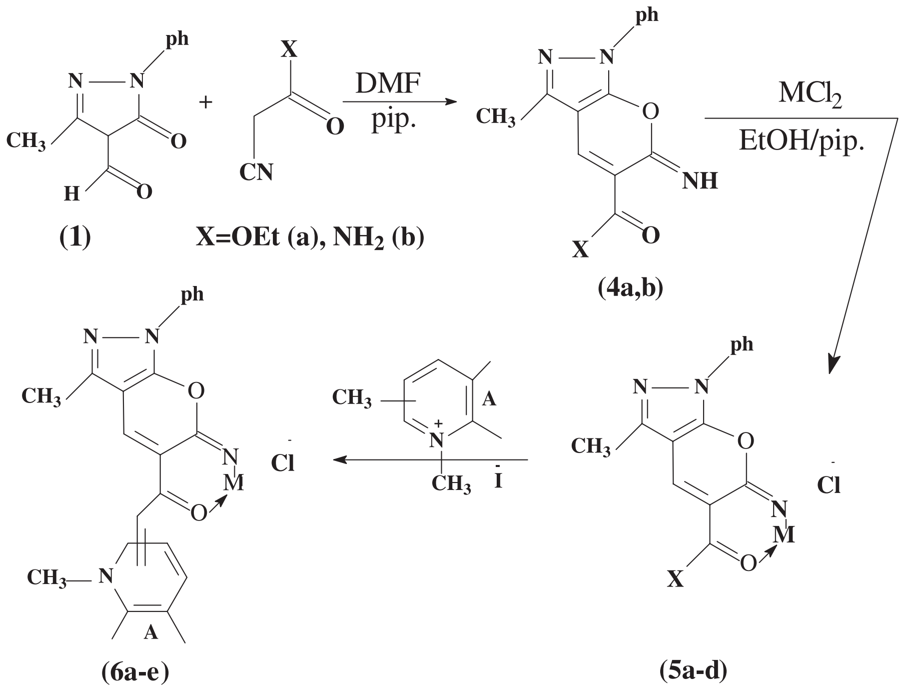
Reaction of 5-acetyl-3-methyl-6-oxo-1-phenyl pyrano[2,3-*c*]pyrazole (**4c**) [15], with ammonium acetate and acetic acid as solvent afforded 5-acetyl-3-methyl-6-oxo-1-phenyl pyrazolo[4,5-*b*]pyridine (**7**). The reaction of equimolar ratios of compound **7** with cobalt dichloride in absolute ethanol and piperidine as a basic catalyst produced 3,5-dimethyl-1-phenylpyrazolo[4,5-*b*]pyridine-7-cobalto-heterocyclic ylide chloride (**8**). Reaction of equimolar ratios of compound **8** with pyridinium, quinolinium and isoquinolinium methiodide in the presence of piperidine produced 3-methyl-1-phenylpyrazolo[4,5-*b*]pyridine-7-cobalto-5[4(1)]-monomethine cyanine dyes (**9a–c**) (Scheme 3).

The formation of 3-methyl-1-phenylpyrazolo[4,5-*b*] pyridine-7-cobalto-5[4(1)]-mono-methine cyanine dyes (**9a–c**) was suggested to proceed as follows:





The structure of compounds **7** to **9a–c** was confirmed by analytical and spectral data. Infrared (IR) spectra of compounds **7–9a** showed general absorption bands at 1520 cm^{-1} (νC=N), 1585 cm^{-1} (νC=C), 520 cm^{-1} (νM–O) and 2940 cm^{-1} (νCH_3I) for compound **9a**. ^1H NMR (DMSO) of compound **7** showed signals at 1.15 ppm (s, 3H, CH_3-pyrazole), 9.75 ppm (s, 1H, NH), 6.85–7.95 ppm (m, 6H, Ar-H + het-H), and signals at 1.19 ppm (s, 3H, CH_3-pyrazole), 3.95 ppm



(5a-d): a) X = OEt, M = Cu; b) X = NH₂, M = Ni; c) X = NH₂, M=Co; d) X = NH₂, M=Cu

(6a-e): a) M = Cu, A = 1-methylquinolin-2-ium; b) M = Ni, A= 1-methylpyridin-2-ium; c) M = Ni, A= 1-methylquinolin-2-ium; d) M = Ni, A= 1-methylpyridin-4-ium; e) M=Co, A= 1-methylquinolin-2-ium

Scheme 2.

(s, 3H, CH_3N^+), 6.52–8.11 ppm (m, 10H, Ar-H + het-H + CH=) for compound **9a**.

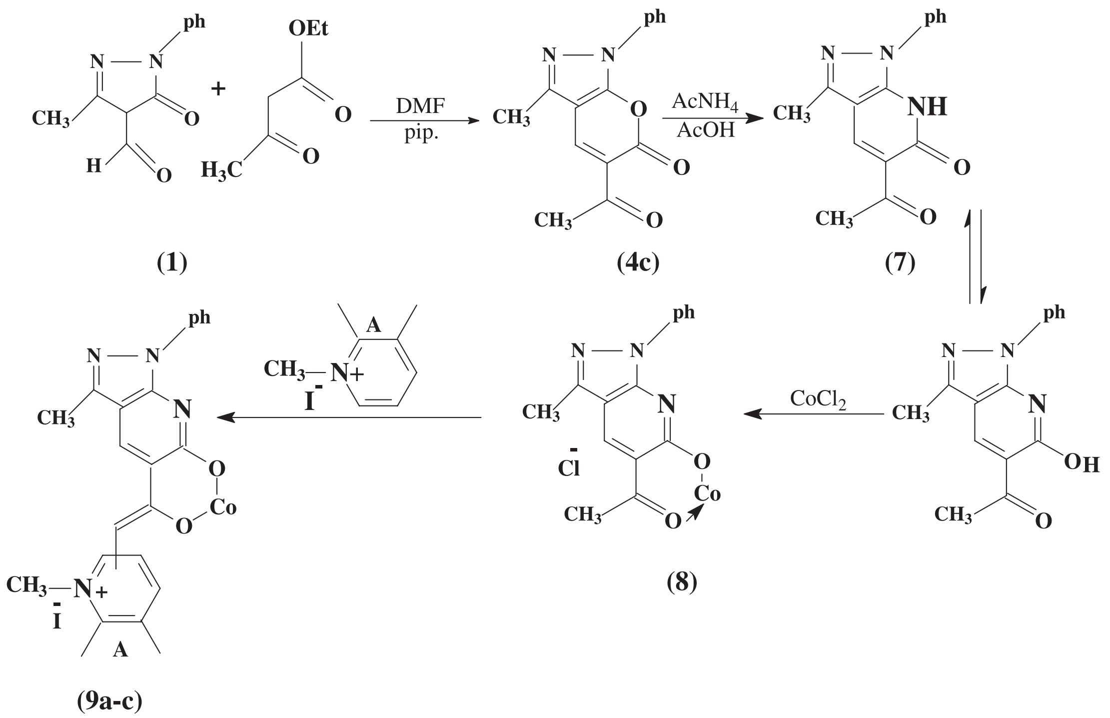
Note: There is a difference in the anions of the synthesized compounds: chlorine in Schemes 1 and 2 for compounds **3a–e** and **6a–e** and iodine in Scheme 3 for compounds **9a–c**. The analysis has shown and confirmed this difference which can be explained as follows.

In the preparation of compounds **3a–e** and **6a–e** (Schemes 1 and 2), the abstraction of halogen anions (chlorine or iodine) is dependent on the basicity and reactivity of the methyl group of the two reactants heterocyclic **2a–c** or **5a–c** and 2(4)-methylheterocyclic quaternary salts. Thus, 2(4)-methylheterocyclic quaternary salts are more basic, have a more reactive methyl group and less stability which leads to the formation of the methylene base with losing HI [16]. On the other hand, in the preparation of compounds **9a–c**, the heterocyclic compound **8**, which contains a methyl group is more reactive and forms the methylene base with the loss of HCl.

The synthesized new monomethine cyanine metal complex dyes **3a–e**, **6a–e** and **9a–c** were soluble in ethanol; their colors in ethanol ranging from reddish violet to intense violet. They were soluble in concentrated H_2SO_4 and did not liberate iodine vapor on warming with the exception of compounds **9a–c** (Scheme 3).

3.2. Relation between molecular structure and electronic absorption spectra of synthesized monomethine cyanine dyes metal complex

The electronic absorption spectral data (λ_{max} and ε_{max} values) of the new monomethine cyanine metal complex dyes are listed in Table 1. The visible absorption spectra of these dyes exhibit various absorption bands within the wavelength range (λ = 350–700 nm). These absorption bands depend primarily on the terminal group (heterocyclic residue A), their linkage position [14], and the type of the transient metal complex of compounds **3a–e** and **6a–e**. Thus, substituting A = 1-methylpyridin-2-ium in compound **3a** with A = 1-methylquinolin-2-ium in compound **3b** gives a bathochromic shift of 65–75 nm with the appearance of new absorption bands located



(**9a-**c): -a) A = N-methylpyridin-4-ium salt; b) A = N-methylquinolin-4-ium saltl;

c) A=N-methylisoquinolin-1-ium salt

Scheme 3.

at $\lambda_{max} = 385$ and 625 nm, respectively (Fig. 1). Substituting A = 1-methylpyridin-2-ium in compound **6a** with A = 1-methylquinolin-2-ium in compound **6b** causes a bathochromic shift of 70 nm. This can be attributed to the more extensive π-delocalization within quinolin-2-ium moiety (Fig. 2).

Changing the linkage position of the pyridinium residue from 2-ium to 4-ium in compounds **3a**, **3c** and **6a**, **6c** resulted in a bathochromic shift. Thus, substituting A = 1-methylpyridin-2-ium in compound **3a** with A = 1-methylpyridin-4-ium in compound **3c** caused a bathochromic shift of 10–35 nm (Fig. 1). Substituting A = 1-methylpyridin-2-ium in compound **6a** with A = 1-methylpyridin-4-ium in compound **6c** caused a bathochromic shift of 25 nm. This is due to increases in the conjugation of the pyridine-4-ium linkage (Fig. 2).

Table 1
Electronic absorption spectra of monomethine metal complex **3a–e**, **6a–e** and **9a–c** cyanine dyes in ethanol

λ_{max} (nm)/log ε_{max} (mol^{-1} cm^{-1})				
Monomethine cyanine dyes (**3a–e**)				
3a	**3b**	**3c**	**3d**	**3e**
–	385 (4.35)	–	–	–
400 (4.15)	475 (6.05)	410 (3.85)	–	–
500 (4.75)	560 (5.17)	525 (4.35)	545 (6.17)	500 (4.55)
–	625 (4.24)	–	650 (4.25)	600 (3.95)
Monomethine cyanine dyes (**6a–e**)				
6a	**6b**	**6c**	**6d**	**6e**
475 (4.17)	445 (5.57)	500 (4.39)	535 (4.47)	415 (3.04)
Monomethine cyanine dyes (**9a–c**)				
9a	**9b**	**9c**		
375 (4.53)	–	–		
430 (4.45)	450 (4.43)	440 (4.35)		
–	540 (3.95)	505 (3.75)		

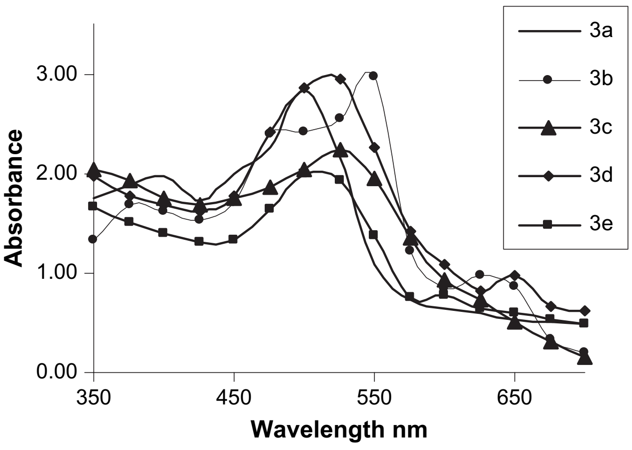


Fig. 1. The electronic absorption spectra of monomethine cyanine dyes (**3a–e**) in ethanol solution in 350–700 nm wavelength.

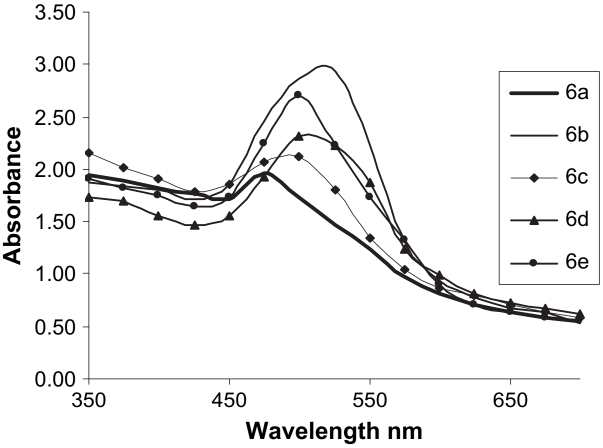


Fig. 2. The electronic absorption spectra of monomethine cyanine dyes (**6a–e**) in ethanol solution in 350–700 nm wavelength.

Additionally, the visible absorption bands of the new monomethine cyanine metal complex dyes **3a–e** and **6a–e** are influenced by the type of metal M. Thus, substituting M = Cu in compound **3e** with M = Co in compound **3d** caused a bathochromic shift of 45 nm with the appearance of new absorption bands located at $\lambda_{max} = 650$ nm. This is due to a vacant orbital, which increases gradually from copper to cobalt leading to the more extensive π-conjugation in compound **3d** (Fig. 1).

The visible absorption bands of the new monomethine cyanine metal complex dyes (**9a–c**) are influenced by the heterocyclic residue A and their linkage position. Substituting of A = 1-methylpyridin-4-ium in compound **9a** by A = 1-methylquinolin-4-ium in compound **9b** resulted in a bathochromic shift of 40–75 nm. This is due to the more extensive π-conjugation in the quinoline moiety (Fig. 3).

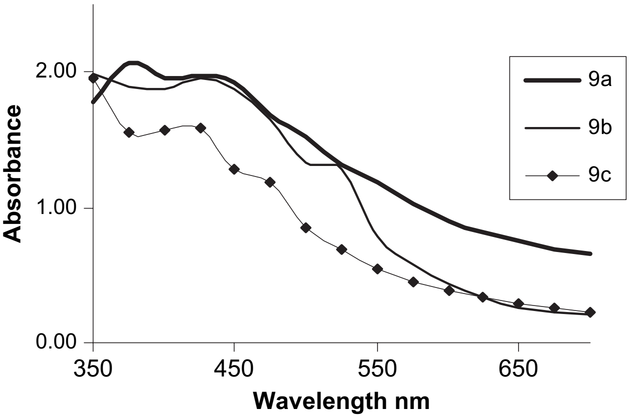


Fig. 3. The electronic absorption spectra of monomethine cyanine dyes (**9a–c**) in ethanol solution in 350–700 nm wavelength.

References

[1] Tatsusuke K, Yasuo, K. JP Patent No 07–70 453; 1995.
[2] Asushi O, Takayuki, I. JP Patent No 06–336 086; 1994.
[3] Atsushi Y, Yasunshi, A. JP Patent No 06–199 045; 1994.
[4] Herz AH. Photogr Sci Eng 1974;18:323.
[5] Armitage B, Retterer J, O'Brien DF. J Phys Soc 1997;101:2602.
[6] Zhifei D, Bixian P. Dyes Pigments 1998;36(2):169–75.
[7] Jonathan EHB, James RY, Harry LA. Chem Commun 2000; 905–6.
[8] Bernhard O, Micheala G, Martin B, Frank L, Mario P, Otto SW. Photochem Photobiol 2001;74(2):237–45.
[9] Frank W, Sheng Y, Tony D, Rüdiger W. J Am Chem Soc 2002; 124:9431–47.
[10] Abd El-Aal RM. Dyes Pigments 2004;61:251–61.
[11] Nakazumi H, Hamada E. J Soc Dyes Colour 1989;105:26.
[12] Kuramoto No. J Soc Dyes Colour 1990;106:181.
[13] Sumiko K, Masahiro S. JP Patent No 06–320 869; 1994.
[14] Rajagopal R, Shenoy VU, Padmanabhan S, Sequeira S, Seshadri S. Dyes Pigments 1990;13:167.
[15] Abd El-Aal RM, Younis M. Dyes Pigments 2004;60:205–14.
[16] Abd El-Aal RM, Koraiem AIM, El-Deen NS. Dyes Pigments 2004;63(3):301–14.