New Mixed Ligand Cobalt(II), Nickel(II) and Copper(II) Complexes of 2,2'-Bipyridine-3,3'-Dicarboxylic acid (bpdc) with 2-Mercapto-5-Phenyl-1,3,4-Oxadiazole (phozSH) and Their Antioxidant activity

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ABSTRACT

The mixing of one mole of 2,2'-bipyridine-3,3'-dicarboxylic acid (bpdc) with two mole of potassium hydroxide (KOH) in methanol were refluxed for (half hour), followed by addition of one mole methanol solution of MCl\textsubscript{2}.nH\textsubscript{2}O (where M=Co, Ni or Cu). The mixture was refluxed for (2 hours) to give colored complexes of the metal ions of [M(bpdc)(H\textsubscript{2}O)\textsubscript{4}]. The [M(bpdc)(H\textsubscript{2}O)\textsubscript{4}] were reacted with one mole of 2-Mercapto-5-phenyl-1,3,4-oxadiazole (phozSH) producing the colored mixed ligand complexes with general formula [M(bpdc)(phozSH)(H\textsubscript{2}O)\textsubscript{3}] in which the metal ions coordinated to the ligand through O-atoms of carboxyl group in (bpdc) and N-atom of (phozSH) ligand. The ligands and complexes are well identified by using Furrier transform infrared spectroscopy, 1\textsuperscript{H}-NMR, 13\textsuperscript{C}-NMR, Electronic spectroscopy, CHNS analysis, Melting point, conductivity measurement. The Antioxidant activity were screened for all the complexes by the use of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method.

Keywords: Cobalt(II), Nickel(II), Copper(II), Bipyridine, Oxadiazole, Mixed Ligand Complexes, Antioxidant activity.

INTRODUCTION

Oxadiazoles have been recognized during a century, nevertheless the majority of research has focused on the symmetric 1, 2, 5- and 1, 3, 4-oxadiazoles\textsuperscript{1}. 1, 3, 4-oxadiazoles and their complexes have fascinated more consideration because of their biological behavior in both agrochemicals and pharmaceuticals\textsuperscript{2}. For example, numerous derivatives of 1, 3, 4-oxadiazoles reveal analgesic\textsuperscript{3}, muscle relaxant, anti-malarial\textsuperscript{4}, anti-inflammatory\textsuperscript{5}, anti-tubercular\textsuperscript{6,7}, fungicides\textsuperscript{8,9}, anti-bacterial\textsuperscript{10,11}, insecticidal, anti-oxidant\textsuperscript{12} and anticancer\textsuperscript{2,13}.

In the present work, we give an account of the preparation and identification of new mixed ligand Co(II), Ni(II) and Cu(II) complexes comprising the two ligands of 2, 2'-bipyridine-3, 3'-dicarboxylic acid (bpdc) and 2-Mercapto-5-phenyl-1,3,4-oxadiazole (phozSH). We found that bpdc ligand behave as a bidentate chelate that connected to the metal centriones by oxygen atom of the carboxyl group while the phozSH ligand work as a monodentate that link to the metal ions by nitrogen atom.
MATERIALS AND METHODS

The (NiCl₂₆H₂O, CoCl₂₆H₂O, CuCl₂₂H₂O, KOH) materials are available in BDH and 2, 2'-bipyridine-3, 3'-dicarboxylic acid, 2-Mercapto-5-phenyl-1,3,4-oxadiazole and 2, 2-diphenyl-1- picrylhydrazyl materials were commercially accessible from Yahoo Chem. China. The FT-IR spectra were registered on a Shimadzu IR- spectrophotometer in the range of 400-4000 cm⁻¹ by utilizing KBr discs. (^1H and ^13C)-NMR spectra were performed on a Bruker 400 MHZ Ultra-shied. UV-Visible spectra were taken on a UV-Visible spectrometer, AE-UV1609 (UK) CO., LTD. The conductivity measurements were estimated on a conductivity meter type Senz μSiemen conductivity tester. CHNS analyses were executed on Euro EA 3000 Elemental Analyzer.

Synthesis of [Co(k²-bpdc)(k¹-phozSH)(H₂O)] (1)

It was synthesized by the following stages

Stage one: Preparation of [Co(k²-bpdc)(H₂O)]

2, 2'-bipyridine-3, 3'-dicarboxylic acid (bpdc) (0.3 millimole, 0.0732 g) was dissolved in methanol (10 milliliter) and (5 milliliter) methanol solution of KOH (0.6 millimole, 0.0336 gram) was added. After refluxing for (30 min), a solution of CoCl₂₆H₂O (0.3 millimole, 0.0713 g) in methanol (5 milliliter) was added dropwise. The resulted solution was heated under reflux for 2 h and filtered. The yellow green precipitate was produced when the filtrate was evaporated at room temperature. (Chemical formula: C₁₅H₁₀CoN₅O₄; Yield: 0.09 gram, 65.7%; Melting point: 230-232°C; Color: dark-green).

Stage two: Reaction of [Co(k²-bpdc)(H₂O)] with (phozSH)

A warm solution of (phozSH) ligand (0.2 millimole, 0.0356 g) in (10 milliliter) ethanol was added to a hot suspended solution of [Co(k²-bpdc)(H₂O)] (0.2 millimole, 0.074 g) in CH₂Cl₂ (10 milliliter). The mixture was heated under reflux for 2 h and filtered. The yellow green precipitate was attained when the solution was evaporated at room temperature.

Yield = 0.09 g, 81%; Melting point: 174-176°C; Color: yellow-green. Anal. Calc. for C₁₅H₁₀CoN₅O₄S: C, 45.02; H, 3.37; N, 10.50; S, 6.01. Found: C, 45.66; H, 4.06; N, 10.10; S, 5.47%. IR (ν max/cm⁻¹): ν(H₂O) 3398; ν(SH) 2953; ν(C=O) 1718; ν(C=N) 1612; ν(C=N of bpdc) 1573; ν(N-N) 1446; ν(C-O-Co) 1076; ν(C-S) 696; ν(M-H₂O) 630; ν(Co-O) 480; ν(Co-N) 443. ^1H NMR (295K, ppm, DMSO-d₆): 7.65-8.9 (m, 11H, phenyl proton of bpdc and phozSH); 2.59 (s, SH proton); 4.14 (s, water proton in DMSO); 39.32 C (DMSO).

Synthesis of [Ni(k²-bpdc)(k¹-phozSH)(H₂O)] complex (2)

It was synthesized by the following stages

Stage one: Preparation of [Ni(k²-bpdc)(H₂O)]

A solution of KOH (0.6 millimole, 0.0336 g) in methanol (5 milliliter) was placed to a solution of bpdc (0.3 millimole, 0.0732 g) in methanol (10 milliliter) and refluxed for (30 minutes). The subsequent mixture was refluxed for a further (2 h) after addition of a methanol solution (5 milliliter) of NiCl₂₆H₂O (0.3 millimole, 0.0713 g) and filtered. When the solution was evaporated at room temperature the dark-green solid was formed. (Chemical formula: C₁₅H₁₀NiN₅O₄; Yield: 0.13 g, 94.3%; Melting point: 230-232°C; Color: dark-green).

Stage two: Reaction of [Ni(k²-bpdc)(H₂O)] with (phozSH)

To a warm stirred solution of [Ni(k²-bpdc)(H₂O)] (0.2 millimole, 0.0743 g) in CH₂Cl₂ (10 milliliter), a hot ethanolic solution (10 milliliter) of phozSH (0.2 millimole, 0.0356 gram) was added and the resultant solution was heated under reflux for 2 h and filtered. The green precipitate was obtained when the solution was evaporated at room temperature.

Yield = 0.08 g, 80%; decomposition point: 210-212°C; Color: green. Anal. Calc. for C₁₅H₁₀NiN₅O₄S: C, 45.04; H, 3.37; N, 10.51; S, 6.01. Found: C, 45.15; H, 3.27; N, 10.33; S, 5.58%. IR (ν max/cm⁻¹): ν(H₂O) 3421; ν(SH) 2852; ν(C=O) 1724; ν(C=N) 1610; ν(C=N of bpdc) 1573; ν(N-N) 1446; ν(C-O-Ni) 1093; ν(C-O-Co) 1076; ν(C-S) 696; ν(Ni-H₂O) 651; ν(Ni-O) 480; ν(Ni-N) 513. ^1H NMR (295K, ppm, DMSO-d₆): 8.4-9.5 (m, 11H, phenyl proton of bpdc and phozSH); 2.55 (s, DMSO proton); 3.49 (s, SH proton); ^13C NMR (DMSO, δ, 400 MHz): 172 C (carboxyl); 150 and 160 C (oxadiazole); 123.96-130.18 C (ph groups of bpdc and phozSH); 39.32 C (DMSO).
Synthesis of $[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$ complex (3)

It was synthesized by the following stages

Stage one: Preparation of $[\text{Cu}(\kappa^2\text{-bpdc})(\text{H}_2\text{O})_4]$

To a methanol solution (10 mL) of bpdc (0.3 millimole, 0.0732 g), a methanol solution (5 milliliter) of KOH (0.6 millimole, 0.0336 g) was added and refluxed for (30 min) then a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.3 millimole, 0.0514 g) dissolved in (5 milliliter) methanol was added and the resultant solution was refluxed for a further 2 h and filtered. The green solid was achieved when the solvent was evaporated at room temperature. (Chemical formula: $\text{C}_{12}\text{H}_{14}\text{CuN}_2\text{O}_8$; Yield: 0.07 g, 61.9 %; Melting point: 236-238°C; Color: green).

Stage two: Reaction of $[\text{Cu}(\kappa^2\text{-bpdc})(\text{H}_2\text{O})_4]$ with (PhozSH)

To a hot suspended solution of $[\text{Cu}(\kappa^2\text{-bpdc})(\text{H}_2\text{O})_4]$ (0.2 millimole, 0.0752 g) in dichloromethane (10 milliliters), a hot solution of phozSH (0.2 millimole, 0.0356 g) in ethanol (10 milliliters) was added and heated under reflux for 2 h then filtered. After the solvent was evaporated at normal temperature the light-green product was achieved.

Yield = 0.10 g, 90 %. Decomposition point: 217-219°C; Color: light-green. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{CuN}_4\text{O}_8\text{S}$: C, 44.64; H, 3.34; N, 10.41; S, 5.96. Found: C, 44.20; H, 3.20; N, 10.51; S, 5.51 %. IR ($\nu_{\text{max}}$/cm$^{-1}$): $\nu(\text{H}_2\text{O})$ 3088; $\nu(\text{SH})$ 2852; $\nu(\text{C}=\text{O})$ 1728; $\nu(\text{C}=\text{N})$ 1610; $\nu(\text{C}=\text{N of bpdc})$ 1571; $\nu(\text{C}=\text{O}-\text{Cu})$ 1097; $\nu(\text{C}=\text{O}-\text{C})$ 1078; $\nu(\text{C}=\text{S})$ 700; $\nu(\text{Cu-H}_2\text{O})$ 638; $\nu(\text{Cu-O})$ 420; $\nu(\text{Cu-N})$ 542. $^1\text{H}$ NMR (295K, ppm, CDCl$_3$): 7.67-8.4 (m, 11H, phenyl proton of bpdc and phozSH); 2.57 (s, DMSO proton); 3.70 (s, SH proton), $^{13}\text{C}$ NMR (DMSO, $\text{d}_6$, 400 MHz): 167 C (carboxyl); 152 and 162 C (oxadiazole); 122-132.08 C (ph groups of bpdc and phozSH); 39.40 C (DMSO).

RESULTS AND DISCUSSION

FT-IR spectra for the synthesized complexes

The IR spectra of Cobalt(II), Nickel(II) and Copper(II) complexes, contain broad band at (3398 and 3421, 3088) cm$^{-1}$ and occurrence of a new weak peaks at (630 and 651 and 638) cm$^{-1}$ were ascribed to $\nu(\text{O-H})$ of coordinated water molecule to the metal ions$^{14}$. The (SH) stretching band at (2567) cm$^{-1}$ of (phozSH) was shifted to a higher frequency to (2953) cm$^{-1}$ in complex 1 and (2852) cm$^{-1}$ in complex 2 and 3$^{15-18}$. A new weak band was appeared at (443, 513, 542) cm$^{-1}$ in the spectra of Cobalt(II), Nickel(II) and Copper(II) complexes were respectively indicated to the linkage of oxadiazole nitrogen to the metal ions. The broad band of (O-H) group of (bpdc) at (2576) cm$^{-1}$ was disappeared in all complexes and a new weak peak was observed at (480, 450 and 420) cm$^{-1}$ were indicated to O-coordination of (bpdc) ligand to (Cobalt(II), Nickel(II) and Copper(II)) metals correspondingly$^{19-22}$. 

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Furthermore, disappearance of the singlet carboxyl protons of (bpdc) ligand at (11.0) ppm indicated the coordination of O-atom of bpdc to Cobalt(II), Nickel(II) and Copper(II) metals. By contrast, the thiol proton of (phozSH) ligand was shifted to a higher chemical shift and appeared at (2.59, 3.49, 3.70) ppm were assigned to N-bound coordination of oxadiazole nitrogen to Co, Ni and Cu(II) metals, respectively.

The $^1$H-NMR spectra of complexes (1-3) displayed an unresolved multiplet signals in the region $\delta$(7.65-8.9), (8.4-9.5) and (7.67-8.4) ppm, were respectively ascribed to aromatic phenyl protons of both (bpdc) and (phozSH) ligands.

The $^{13}$C-NMR spectral data of the prepared complexes were estimated in DMSO-d$_6$ solvent. In the spectra of (1-3) complexes, the carboxyl carbon atoms of (bpdc) ligand observed in the regions (175.53, 172 and 167) ppm respectively, while the two oxadiazole carbon atoms of (phozSH) ligand were occurred at $\delta$(158 and 168), (150 and 160)
and (152 and 162) ppm respectively. The aromatic phenyl carbon atoms of both bpdc and phozSH correspondingly occurred within (120.57-130.49), (123.96-130.18) and (122-132.08) ppm.

**Elemental analysis for the synthesized complexes**

The elemental analysis (C, H, N, S) data for all the synthesized complexes are listed in Table 1. These numbers are coherent with the proposed stoichiometries. Other physical properties such as colors, molecular weight (M.Wt.) and melting points (M. P.) of the synthesized complexes are also written.

**Table 1: Colors, M.Wt., M.P. and (CHNS) analysis for the synthesized complexes**

| No. | Synthesized compounds | Color         | M.Wt g/mol | M.P. (°C) | (Calculated) Found % |
|-----|----------------------|---------------|------------|-----------|---------------------|
| 1   | [Co(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] | yellow-green | 533        | 174-176   | (45.02) (3.37) (10.5) (6.01) |
| 2   | [Ni(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] | Green        | 532.75     | d.p. 210-212 | (45.04) (3.37) (10.51) (6.01) |
| 3   | [Cu(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] | light-green  | 537.6      | d.p. 217-219 | (44.64) (3.34) (10.41) (5.96) |

**Electronic Spectra for the Prepared Complexes**

The electronic spectra of (bpdc and phozSH) ligands were performed in ethanol and their synthesized complexes in DMSO solvent. The UV-Vis. spectra of bpdc and phozSH ligands displayed two absorption peaks at (41666, 37037) and (40000, 33333) cm⁻¹, these transitions were correspondingly ascribed to π-π* and n-π* transitions. The spectrum of Co(II) complex (1), showed three bands in the UV-Visible region at 14925, 16393 and 28571 cm⁻¹, were due to 4T₁g(F)→4T₂g(P), 4T₁g(F)→4A₂g and 4T₁g(F)→4T₂g(P) transitions, respectively.

The spectrum of Ni(II) complex (2) exhibited two d-d transitions at 23809 and 30303 cm⁻¹ were respectively attributed to 1A₁g→2A₁g and 1A₁g→1B₁g, and the Cu(II) complex also exhibit two transition bands at 23809 and 29411 cm⁻¹ were due to 2B₁g→2A₁g and 2B₁g→2B₂g transitions. The electronic transitions for all metal complexes indicate an octahedral geometry (Table 2).

**Table 2: Electronic spectral bands of the ligands and their metal complexes**

| Compounds | Absorption band nm | Assignment Transition |
|-----------|--------------------|-----------------------|
| bpdc      | 240 41666          | π → π*                |
|           | 270 37037          | n → π*                |
| phozSH    | 250 40000          | π → π*                |
|           | 300 33333          | n → π*                |
| 1         | 350 28571 (v₁)     | 1T₁g(F)→1T₂g(P)       |
|           | 610 16393 (v₂)     | 1T₁g(F)→1A₁g           |
|           | 670 14925 (v₃)     | 1T₁g(F)→1T₂g          |
| 2         | 330 30303 (v₁)     | 1A₁g→1B₁g             |
|           | 420 23809 (v₂)     | 1A₁g→1A₁g             |
| 3         | 340 29411 (v₃)     | 2B₁g→2A₁g             |
|           | 420 23809 (v₄)     | 2B₁g→2B₂g             |
Fig. 12. Electronic spectrum of bpdc ligand

Fig. 13. Electronic spectrum of phozSH ligand

Fig. 14. Electronic spectrum of $[\text{Co}(\kappa^2-\text{bpdc})(\kappa^1-\text{phozSH})(\text{H}_2\text{O})_3]$ (a) UV. (b) Vis. Region

Fig. 15. Electronic spectrum of $[\text{Ni}(\kappa^2-\text{bpdc})(\kappa^1-\text{phozSH})(\text{H}_2\text{O})_3]$ (a) UV. (b) Vis. Region

Fig. 16. Electronic spectrum of $[\text{Cu}(\kappa^2-\text{bpdc})(\kappa^1-\text{phozSH})(\text{H}_2\text{O})_3]$ (a) UV. (b) Vis. Region
Molar conductivity for the synthesized complexes

The molar conductivities of the synthesized complexes (1-3) were taken for (10^{-3} M) solution in DMSO at (25°C). It was deduced that all the synthesized complexes are non-electrolyte as demonstrated in Table 3.

### Table 3: Molar conductivity (cm^2. ohm^-1. mol^-1) of (10^{-3} M) solution in DMSO for the synthesized complexes

| No. | Complexes | Molar conductivity (cm^2. ohm^-1. mol^-1) |
|-----|-----------|------------------------------------------|
| 1   | [Co(κ²-bpdc)(κ¹-phozSH)(H_2O)_3] | 17                                       |
| 2   | [Ni(κ²-bpdc)(κ¹-phozSH)(H_2O)_3] | 25                                       |
| 3   | [Cu(κ²-bpdc)(κ¹-phozSH)(H_2O)_3] | 20                                       |

Antioxidant assay (DPPH free radical scavenging activity)

The metal complexes were monitored for free radical scavenging activity by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method.

The different concentrations of the tested complexes (25, 50, 75 ppm) and standard vitamin-C were received in separate test tubes, and by addition of DMSO solvent the volume of each tube was settled to 2 milliliter. To all sample solution tubes in DMSO, a methanolic solution of DPPH (2 milliliter). The tubes were permitted to stand for 30 minute. The control experiment was fulfilled by the same method but without the addition of test samples. The absorbance was taken at 517 nm. Radical scavenging activity was calculated by the subsequent formula:\[^{30,31}]

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\% \text{ Radical scavenging activity} = \frac{\text{Absorbance of control OD} - \text{Absorbance of sample OD}}{\text{Absorbance of control OD}} \times 100
\]

The results of free radical scavenger activity of the tested compounds at various concentrations are exhibited in Fig. 17. All complexes 1–3 showed comparable or slightly lower activity than the standard, ascorbic acid.

Co(II), Cu(II) complexes have demonstrated a good free radical scavenging activity with (IC_{50} = 0.920, 5.075 \, \mu \text{mol dm}^{-1}) were the most effective than Ni(II) complex, Fig. 18. Whereas Nickel(II) complex with (IC_{50} = 31.683 \, \mu \text{mol dm}^{-1}) has showed less activity. The metal complexes of Copper(II), Cobalt(II) were displayed higher scavenging activity than the standard, while Ni(II) complex has lower activity than ascorbic acid. The synthesized complexes scavenged the DPPH radical in a concentration dependent manner.
CONCLUSION

This work comprises synthesis of new mixed ligand Cobalt(II), Nickel(II) and Copper(II) complexes with 2-Mercapto-5-phenyl-1,3,4-oxadiazole and 2,2'-bipyridine-3,3'-dicarboxylic acid ligands. Based upon Infrared, UV-Visible, $^1$H-NMR, $^{13}$C-NMR and (CHNS) analysis, we concluded that all the prepared complexes have an octahedral shape in which (bpdc) ligand coordinated to the metals through oxygen atoms, whereas the phozSH ligand connected to the metals via oxadiazole nitrogen atom. In accordance with the molar conductivity data, it has been recommended that all complexes are non-electrolyte. Finally, on the basis of Antioxidant assay, in which metal complexes were screened for free radical scavenging activity by the 2,2-diphenyl-1-picylhydrazyl (DPPH) method, it can be conclude that all the Cobalt(II), Nickel(II) and Copper(II) complexes have a good free radical scavenging activity.

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Conflicts of Interest

The authors declare no conflict of interest.

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