



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 $MCl_2 \cdot nH_2O$ (where M=Co, Ni or Cu). The mixture was refluxed for (2 hours) to give colored complexes of the metal ions of $[M(bpdc)(H_2O)_4]$. The $[M(bpdc)(H_2O)_4]$ were reacted with one mole of 2-Mercapto-5-phenyl-1,3,4-oxadiazole (phozSH) producing the colored mixed ligand complexes with general formula $[M(bpdc)(phozSH)(H_2O)_3]$ 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 Fourier transform infrared spectroscopy, ¹H-NMR, ¹³C-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-oxadiazoles¹. 1, 3, 4-oxadiazoles and their complexes have fascinated more consideration because of their biological behavior in both agrochemicals and pharmaceuticals². For example, numerous derivatives of 1, 3, 4-oxadiazoles reveal analgesic³, muscle relaxant, anti-malarial⁴, anti-inflammatory⁵, anti-tubercular^{6,7}, fungicides^{8,9}, anti-bacterial^{10,11},

insecticidal, anti-oxidant¹² and anticancer^{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 bpydc ligand behave as a bidentate chelate that connected to the metal centre ions 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 (NiCl₂·6H₂O, CoCl₂·6H₂O, CuCl₂·2H₂O, 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-shield. 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(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] (1)

It was synthesized by the following stages

Stage one: Preparation of [Co(κ²-bpdc)(H₂O)₄]

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 CoCl₂·6H₂O (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 light brown precipitate was produced when the filtrate was evaporated at room temperature. (Chemical formula: C₁₂H₁₄CoN₂O₈; Yield: 0.09 gram, 65.7%; decomposition point: 296°C; Color: light brown).

Stage two: Reaction of [Co(κ²-bpdc)(H₂O)₄] 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(κ²-bpdc)(H₂O)₄] (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 C₂₀H₁₈CoN₄O₈S: 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-O-C) 1062; 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), ¹³C NMR (DMSO, δ, 400 MHz): 175 C (carboxyl); 158 and 168 C (oxadiazole); 120.57-130.49 C (ph groups of bpdc and phozSH); 39.38 C (DMSO).

Synthesis of [Ni(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] complex (2)

It was synthesized by the following stages

Stage one: Preparation of [Ni(κ²-bpdc)(H₂O)₄]

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 NiCl₂·6H₂O (0.3 millimole, 0.0713 g) and filtered. When the solution was evaporated at room temperature the dark-green solid was formed. (Chemical formula: C₁₂H₁₄NiN₂O₈; Yield: 0.13 g, 94.3%; Melting point: 230-232°C; Color: dark-green).

Stage two: Reaction of [Ni(κ²-bpdc)(H₂O)₄] with (PhozSH)

To a warm stirred solution of [Ni(κ²-bpdc)(H₂O)₄] (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 C₂₀H₁₈NiN₄O₈S: 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-C) 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 $[\text{Cu}(\kappa^2\text{-bpdc})(\text{H}_2\text{O})_4]$

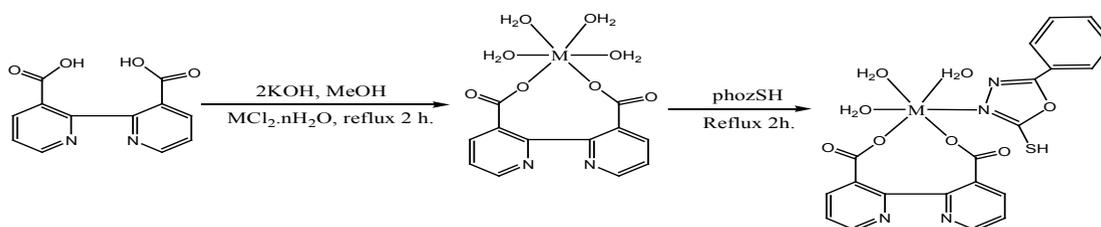
To a methanol solution (10 mL) of bpdc (0.3 millimole, 0.0732 g), a methanol solution (5 milliliter) of KOH (0.6 millimole, 0.0336 g) was added and refluxed for (30 min) then a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.3 millimole, 0.0514 g) dissolved in (5 milliliter) methanol was added 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 $[\text{Cu}(\kappa^2\text{-$

$\text{bpdc})(\text{H}_2\text{O})_4]$ (0.2 millimole, 0.0752 g) in dichloro methane (10 milliliter), a hot solution of phozSH (0.2 millimole, 0.0356 g) in ethanol (10 milliliter) 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 ($\nu_{\text{max}}/\text{cm}^{-1}$): $\nu(\text{H}_2\text{O})$ 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; $\nu(\text{Cu}-\text{H}_2\text{O})$ 638; $\nu(\text{Cu}-\text{O})$ 420; $\nu(\text{Cu}-\text{N})$ 542. ^1H 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}C NMR (DMSO, δ , 400 MHz): 167 C (carboxyl); 152 and 162 C (oxadiazole); 122-132.08 C (ph groups of bpdc and phozSH); 39.40 C (DMSO).



Scheme 1. Synthesis of $[\text{M}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$, where M=Cobalt, Nickel or Copper(II)

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 $\nu(\text{O}-\text{H})$ of coordinated water molecule to the metal ions¹⁴. 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 3¹⁵⁻¹⁸. 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 correspondingly¹⁹⁻²².

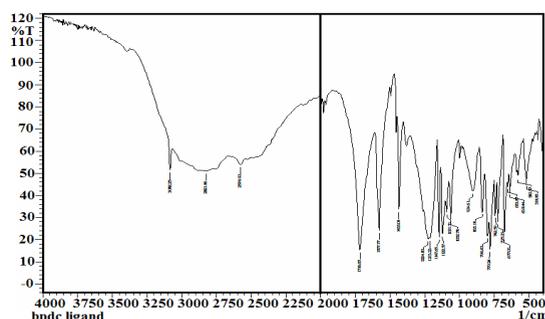


Fig. 1. IR spectrum of bpdc ligand

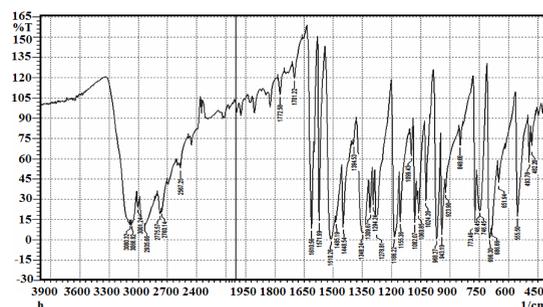


Fig. 2. IR spectrum of phozSH ligand

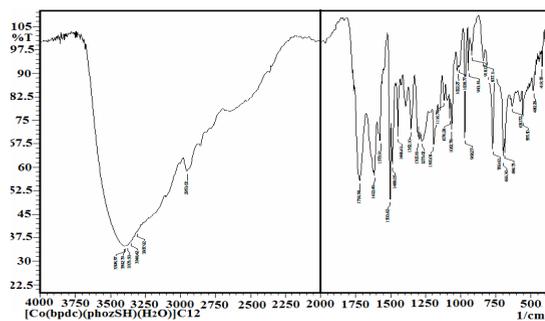


Fig. 3. IR spectrum of $[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$ complex

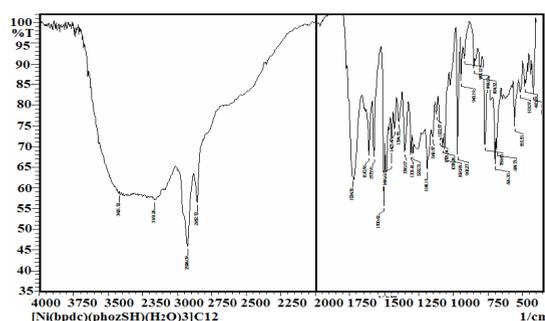


Fig. 4. IR spectrum of $[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$ complex

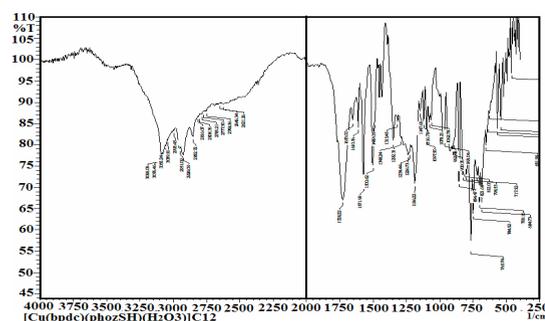


Fig. 5. IR spectrum of $[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$ complex

¹H-NMR Spectra for the synthesized Complexes

The ¹H-NMR spectra of (1, 2) complexes have been recorded in DMSO-d⁶ and complex (3) in CDCl₃ solvent. The assignment of all signals have been attained by comparing the ¹H-NMR spectra of the ligands registered in literature. Each sort of signal has a particular chemical shift range that can be applied for initial assignment.

The ¹H-NMR spectra of complexes (1-3) displayed an unresolved multiplet signals in the region δ(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.

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, respectively²³⁻²⁶.

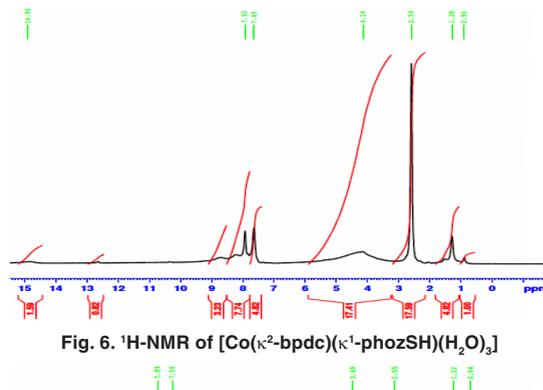


Fig. 6. ¹H-NMR of $[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$

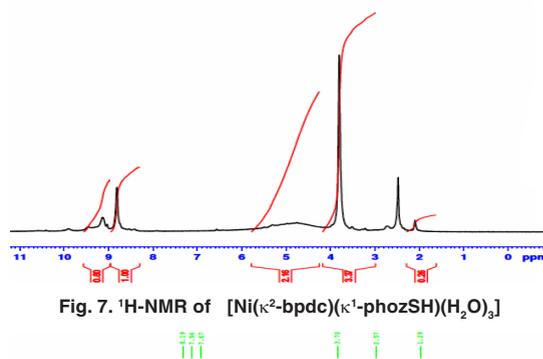


Fig. 7. ¹H-NMR of $[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$

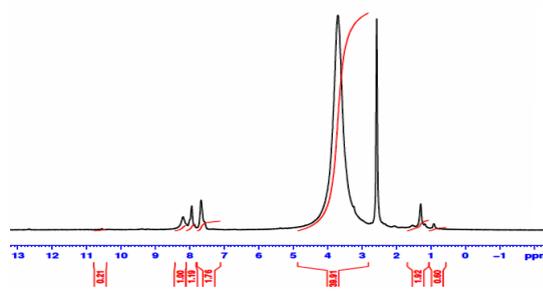


Fig. 8. ¹H-NMR of $[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$

¹³C-NMR Spectra for the synthesized Complexes

The ¹³C-NMR spectral data of the prepared complexes were estimated in DMSO-d⁶ 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 δ(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) ppm²⁵⁻²⁷.

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.

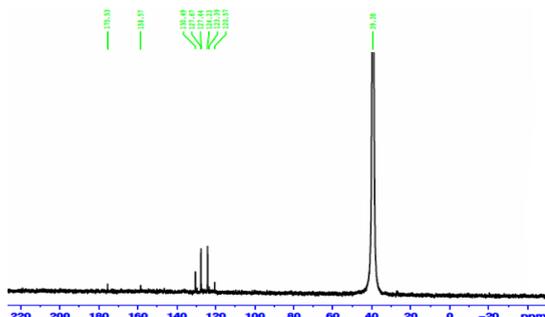


Fig. 9. ¹³C-NMR of [Co(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] complex

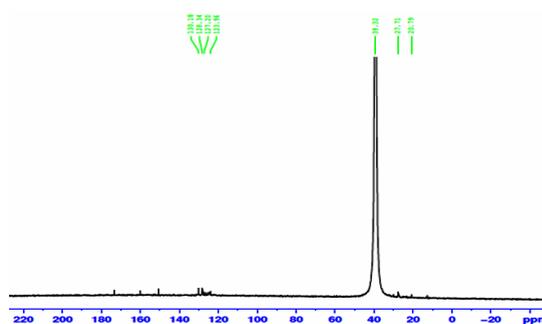


Fig. 10. ¹³C-NMR of [Ni(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] complex

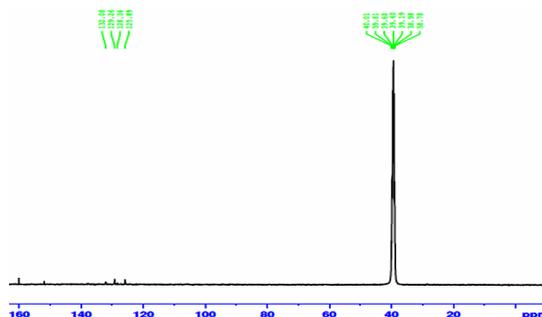


Fig. 11. ¹³C-NMR of [Cu(κ²-bpdc)(κ¹-phozSH)(H₂O)₃] complex

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 %			
					C	H	N	S
1	[Co(κ ² -bpdc)(κ ¹ -phozSH)(H ₂ O) ₃]	yellow-green	533	174-176	(45.02)	(3.37)	(10.5)	(6.01)
					45.66	4.06	10.1	5.47
2	[Ni(κ ² -bpdc)(κ ¹ -phozSH)(H ₂ O) ₃]	Green	532.75	d.p. 210-212	(45.04)	(3.37)	(10.51)	(6.01)
					45.15	3.27	10.33	5.58
3	[Cu(κ ² -bpdc)(κ ¹ -phozSH)(H ₂ O) ₃]	light-green	537.6	d.p. 217-219	(44.64)	(3.34)	(10.41)	(5.96)
					44.20	3.40	10.51	5.51

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 ⁴T_{1(g(F))}→⁴T_{2g}, ⁴T_{1(g(F))}→⁴A_{2g} and ⁴T_{1(g(F))}→⁴T_{2g(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 ¹A_{1g}→¹A_{2g} and ¹A_{1g}→¹B_{1g}, and the Cu(II) complex also exhibit two transition bands at 23809 and 29411 cm⁻¹ were due to

²B_{1g}→²A_{1g} and ²B_{1g}→²B_{2g} transitions. The electronic transitions for all metal complexes indicate an octahedral geometry (Table 2)^{28,29}.

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

Compounds	Absorption band nm	cm ⁻¹	Assignment Transition
bpdc	240	41666	π → π*
	270	37037	n → π*
phozSH	250	40000	π → π*
	300	33333	n → π*
1	350	28571 (v ₃)	⁴ T _{1(g(F))} → ⁴ T _{2g(P)}
	610	16393 (v ₂)	⁴ T _{1(g(F))} → ⁴ A _{2g}
	670	14925 (v ₁)	⁴ T _{1(g(F))} → ⁴ T _{2g}
2	330	30303 (v ₂)	¹ A _{1g} → ¹ B _{1g}
	420	23809 (v ₁)	¹ A _{1g} → ¹ A _{2g}
3	340	29411 (v ₂)	² B _{1g} → ² B _{2g}
	420	23809 (v ₁)	² B _{1g} → ² A _{1g}

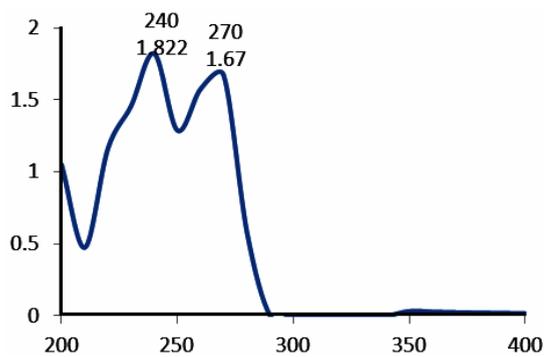


Fig. 12. Electronic spectrum of bpdc ligand

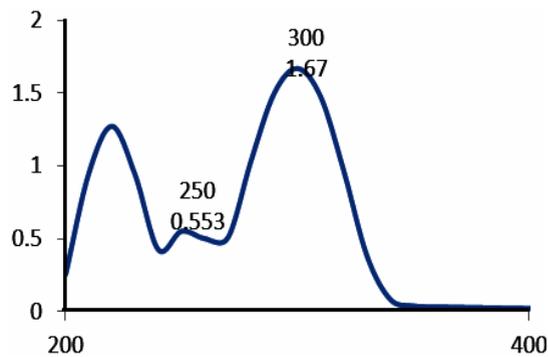
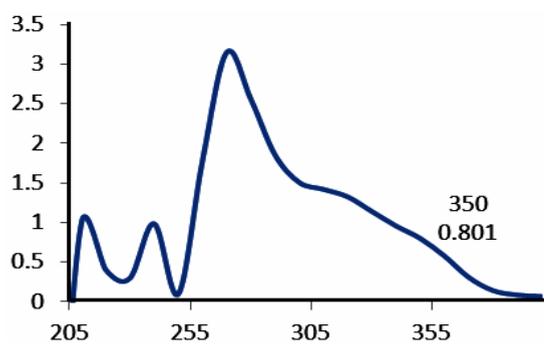
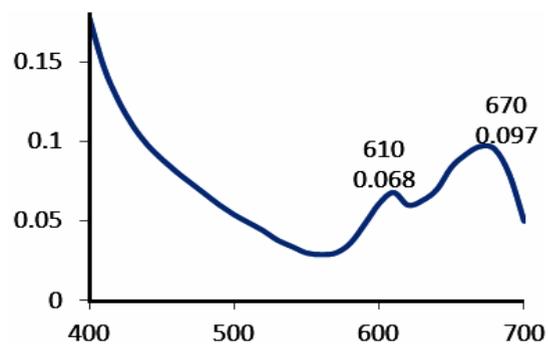


Fig. 13. Electronic spectrum of phozSH ligand

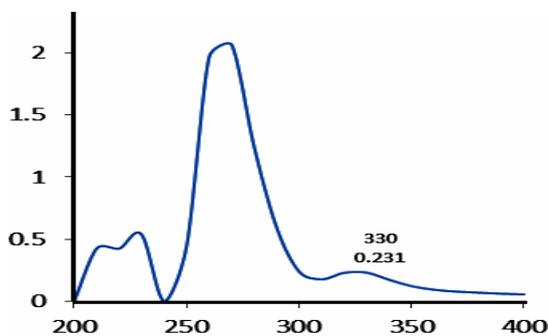


(a)

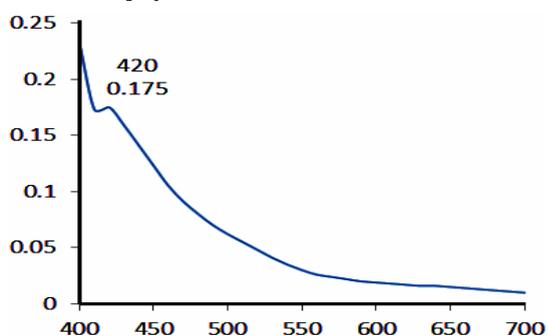


(b)

Fig. 14. Electronic spectrum of $[Co(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(H_2O)_3]$ (a) UV. (b) Vis. Region

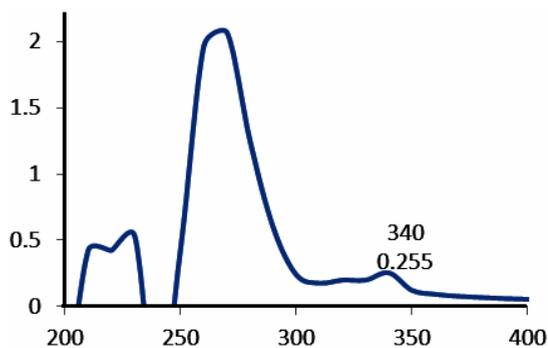


(a)

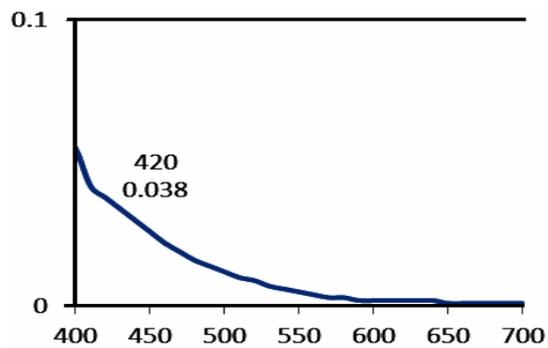


(b)

Fig. 15. Electronic spectrum of $[Ni(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(H_2O)_3]$ (a) UV. (b) Vis. Region



(a)



(b)

Fig. 16. Electronic spectrum of $[Cu(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(H_2O)_3]$ (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 ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$) of (10^{-3} M) solution in DMSO for the synthesized complexes

No.	Complexes	Molar conductivity ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$)
1	$[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	17
2	$[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	25
3	$[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	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}.

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

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 ($\text{IC}_{50} = 0.920, 5.075 \delta \text{ mol dm}^{-1}$) were the most effective than Ni(II) complex, Fig. 18. Whereas Nickel(II) complex with ($\text{IC}_{50} = 31.683 \delta \text{ mol dm}^{-1}$) 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.

Table 4: Absorbance of compounds at different concentration at 517 nm

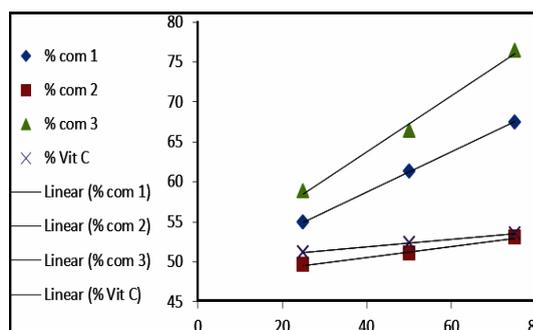
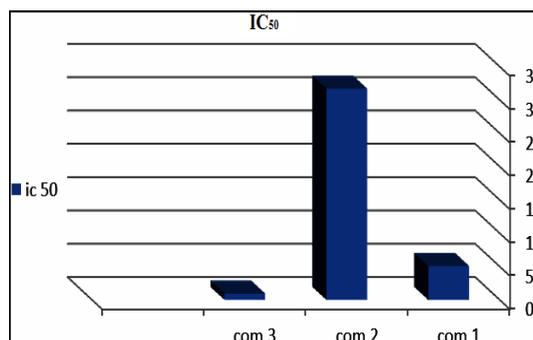
Com. No.	Compound	Concentration ($\mu\text{g/mL}$)		
		25	50	75
	Ascorbic acid (AA)	0.857	0.837	0.816
Com.1	$[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	0.791	0.679	0.571
Com.2	$[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	0.884	0.860	0.824
Com.3	$[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	0.722	0.589	0.413

Table 5: Antioxidant activity of the metal complexes at different concentration using DPPH assay

Com. No.	Compound	Concentration ($\mu\text{g/mL}$)		
		25	50	75
	Ascorbic acid (AA)	51.195	52.334	53.53
Com.1	$[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	54.954	61.332	67.482
Com.2	$[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	49.658	51.025	53.075
Com.3	$[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	58.883	66.457	76.48

Table 6: Superoxide dismutase activity of the prepared complexes

Com. No.	Complexes	IC_{50} ($\mu \text{ mol dm}^{-1}$)
Com. 1	$[\text{Co}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	5.075818
Com. 2	$[\text{Ni}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	31.683
Com. 3	$[\text{Cu}(\kappa^2\text{-bpdc})(\kappa^1\text{-phozSH})(\text{H}_2\text{O})_3]$	0.92

**Fig. 17. Scavenging activity of compounds 1–3 for DPPH****Fig. 18. IC_{50} of compounds 1–3 for DPPH**

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, ¹H-NMR, ¹³C-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-picrylhydrazyl (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.

REFERENCES

- Da Silva, A.; De Silva, M.; Carvalho, C.; Antunes, O.; Herreeea, J.; Brinn, I.; Mangrich, A. *Inorganica chimica acta.*, **1999**, *292*, 1-6.
- Subhi, A.; Ilham, N.; Lamaan, J.; Ayad, H. *Transition metal chemistry.*, **2002**, *27*, 191-195.
- Toma, A.; Hapau, D.; Vlase, L.; Mogosan, C.; Zaharia, V. *Clujul Medical.*, **2013**, *86*, 34-39.
- Kumar, K.; Jayarooma, P.; Kumar, G. *International Journal of Chem Tech Research.*, **2012**, *4*, 1782-1791.
- Husain, A.; Ajmal, M. *Acta. pharmaceutica.*, **2009**, *59*, 223-233.
- Kerur, S.; Alagawadi, K.; Zhu, H.; Manvi, F. *World Journal of Pharmacy and Pharmaceutical Sciences.*, **2014**, *3*, 573-585.
- Pattan, S.; Rabara, P.; Pattan, J.; Bukitagar, A.; Wakale, V.; Musmade, D. *Indian journal of chemistry. Section B, Organic including medicinal.*, **2009**, *48*, 1453.
- Somashekhar, M.; Sonnad, B.; Tare, B.; Heralagi, R.; Lokapure, S. *International Journal of Medicine and Pharmaceutical Research.*, **2014**, *2*, 560-569.
- Kumar, S. *Turkish Journal of Chemistry.*, **2011**, *35*, 99-108.
- Jha, K.; Samad, A.; Kumar, Y.; Shaharyar, M.; Khosa, R.; Jain, J.; Bansal, S. *Iranian Journal of Pharmaceutical Research.*, **2009**, *8*, 163-167.
- Deshmukh, R.; Jha, A.; Thakur, A.; Dewangan, D. *International Journal of Research in Pharmaceutical and Biochemical. Sciences.*, **2011**, *2*, 215-219.
- Rajasekaran, S.; Rao, G.; Chatterjee, A. *International Journal of Drug Development and Research.*, **2012**, *4*, 303-309.
- Adimule, V.; Medapa, S.; Kumar, L.; RAao, P. *Int. J. Drug Dev. and Res.*, **2014**, *6*, 188-195.
- V Gina, V.; Mariana, C.; Coralia, B.; Crina, K.; Lumini, M.; Constantin, G.; Catalin, M.; Larisa, C.; Rodica, O.; Mihaela, B. *Molecules.*, **2018**, *23*, 10.
- Rehab, A.; Zainab, A. *Al- Mustansiriya J. Sci.*, **2009**, *20*, 23.
- Raghad, H.; Emad, Y.; Ahmed A. *Springer Plus.*, **2013**, *2*, 3.
- Buttrus, N.; Mohamed, S. *Research Journal of Chemical Sciences.*, **2013**, *3*, 56.
- Venu, K.; Siva, P.; Ashok, P.; Rameshbabu, K.; Sreeramulu, J. *Journal of Chemical and Pharmaceutical Research.*, **2013**, *5*, 52.
- Zainab, M.; Hameedi, N. *A Multifaceted review Journal in the field of pharmacy.*, **2020**, *11*, 840.
- Mahasin, A.; Sahar, I.; Souad, A. *Journal of Al-Nahrain University.*, **2015**, *18*, 30.
- Chandrakeka, S.; Chandramohan, G. *African journal of pure and applied chemistry.*, **2014**, *8*, 167.
- Saravana, P.; Tharmaraj, P.; Muthuraj, V.; Umadevi, M. *International Journal Of Engineering And Science.*, **2013**, *2*, 16-25.
- Kitagawa, S.; Munakata, M. *Inorganic Chemistry.*, **1981**, *20*, 2261-2267.
- Venu, K.; Siva, P.; Ashok, P.; Rameshbabu, K.; Sreeramulu, J. *Journal of Chemical and Pharmaceutical Research.*, **2013**, *5*, 50-59.

25. Gudasi, K.; Patil, M.; Vadavi, R.; Shenoy, R.; Patil, S. *J. Serb. Chem. Soc.*, **2007**, *72*, 357–366.
26. Ibraheem, H.; Adel, H.; Ahmed, A.; Salih, N.; Salimon, J.; Graisa, A.; Farina, Y.; Yousif, E. *Journal of Al-Nahrain University.*, **2010**, *13*, 43-47.
27. Panagiotis, N.; Dafnopoulos, K.; Tortopidis, C.; Koumbis, A.; Koffa, M.; Psomas, G.; Fylaktakidou, K. *Journal of Photochemistry & Photobiology, B: Biology.*, **2016**, *158*, 30–38.
28. Hoda, A.; Abdel-Nasser, M.; Mutlak S. *Int. J. Electrochem. Sci.*, **2013**, *8*, 9406.
29. Sutton, D. *Electronic spectra of Transition metal complexes: an Introductory text.* McGraw-Hill., **1968**, 73-193.
30. Subarani, R.; Metilda, P. *International Journal of Scientific & Engineering Research.*, **2017**, *8*, 337.
31. Karekal, M.; Bennikallu, H. *Journal of Saudi Chemical Society.*, **2017**, *21*, 202.