



Synthesis, Spectroscopic characterization of Co(II), Ni(II) and Cu(II) complexes with 2-mercapto-5-(2,4-dinitrophenyl)-1,3,4-oxadiazole or 2-mercapto-5-((4-(dimethylamino)benzylidene)amino)-1,3,4-thiadiazole ligands

SALEH A. AHMED¹ and AHMED S. M. AL-JANABI^{2*}

¹Tikrit University College of Pharmacy, Department of Chemistry, Tikrit, Iraq.

²Tikrit University College of Veterinary Medicine, Department of Biochemistry, Tikrit, Iraq.

*Corresponding author E-mail: a_sh200683@yahoo.com

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ABSTRACT

New Co(II), Ni(II) and Cu(II) complexes with 2-mercapto-5-(2,4-dinitrophenyl)-1,3,4-oxadiazole (IpotH) or 2-mercapto-5-((4-(dimethylamino)benzylidene)amino)-1,3,4-thiadiazole (daptH) ligands, were prepared by treatment two moles of thione ligands with one mole of metal salts in EtOH/Acetone and H₂O as a solvents, to afforded octahedral complexes of the types [MX₂(κ²-IpotH)₂] (Where M = Co, Cu, X= Cl and M= Ni, X= NO₃) or [MX₂(κ²-daptH)₂] (Where M = Co, Cu, X= Cl and M= Ni, X= NO₃). The thione ligands bonded through the nitrogen atom of heterocyclic and sulfur atom of thiol group. The prepared ligands and its complexes were characterization by elemental analysis (CHNM), IR spectroscopy, molar conductivity, magnetic susceptibility, UV-Visible spectroscopy and ¹H NMR data.

Keywords: Thione, Thiol, Oxadiazole, Triazole, Complex.

INTRODUCTION

The reaction of transition metal ions with thiones compounds have been the subject of various characterization as these chemical compounds contain active groups [NH-CS ↔ -N=C(SH)], and are helpful parent compounds for S including peer of heterocyclic bases¹⁻⁵. The (thiadiazole or oxadiazole)-thione ligands have many coordinate model with

metal ions, such as S, N as monodentate, or S and N as chelate bidentate, N, S-bridging³⁻⁶. The heavy metals such as Pt(II), Pd(II) and Ag(I) were interacted with nitrogen and sulfur donor atoms have been known for its anticancer against with possibility to improve metal-based drugs¹⁻⁴. The coordination properties of N and S including heterocyclic ligands, such as triazoles, oxadiazoles, is an emerging and rapidly developing area of research⁵⁻¹⁴.



Recently, many research works involving M(II) ions with thiones have been published¹⁵⁻²⁰. In the present work, we report the preparation of Co(II), Ni(II) and Cu(II) complexes with new thione ligands.

EXPERIMENTAL

Methods and Materials

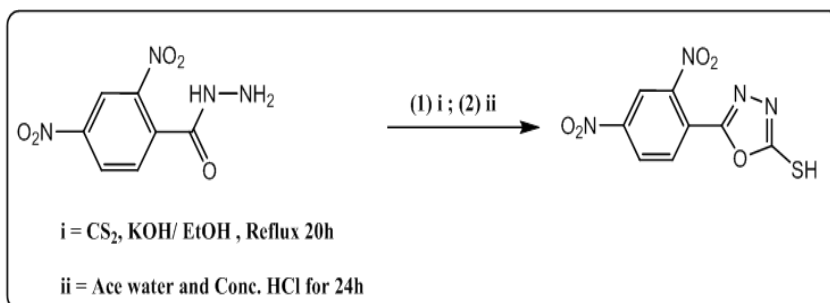
The MX_2 (Where M = Co, Cu, X= Cl and M= Ni, X= NO_3), and organic compounds were provided from Sigma-Aldrich, Fluka, or BDH companies, and used without further purification, Melting points were measured on an SMP40/Stuart Company, The conductivity of 10^{-3} M of DMSO or DMF solutions of prepared complexes were measured at 25°C using Digital conductivity meter. The infrared spectra of prepared ligands and its complexes were recorded with KBr disc in the 4000–400 cm^{-1} range on Shimadzu 8400S FTIR Spectrophotometer. The Ultra violet visible data of prepared compounds were measured on Shimadzu UV-1800 Spectrophotometer in 200-1100 nm using DMSO as a solvent. Magnetic

properties were carried out at 25°C by Bucker BM6 instrument applying Faraday method. CHN element contents were determined by Eurovectro EA 3000/Italy. The ^1H NMR spectra were recorded on Bucker/300 MHz spectrometer with DMSO-d_6 as solvent and Me4Sias internal reference. Metal content was determined on Shimadzu SMP30.

Preparation of ligands

Preparation of 2-mercapto-5-(2,4-dinitrophenyl)-1,3,4-oxadiazole (Ipoth)

A gradual addition of CS_2 (0.076g; 0.001 mol) to a mixture of 2,4-dinitrobenzohyrazide (2.200 g; 0.001 mmol) and KOH (0.560 g; 0.001mol) in EtOH (10 ml) with stirring. The mixture was refluxed for 20 hour. The solvent was evaporated to half under vacuum, and ice to the reduced mixture was added, and followed by add of conc. HCl with cooling, and left at room temperature to complete the precipitate process. The yellow ppt. was filtered off, washed with H_2O and dried in oven under vacuum (Yield: 74%, m.p. 170-173°C) (Scheme 1).

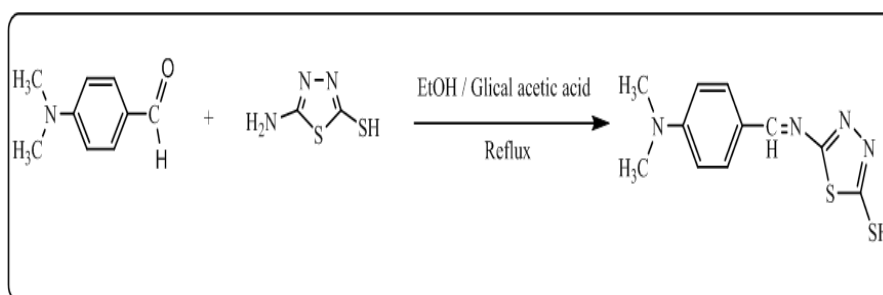


Scheme 1. Preparation of Ipoth ligand

Preparation of 2-mercapto-5-((4-(dimethylamino)benzylidene)amino)-1,3,4-thiadiazole (daptH)

To an ethanoic solution of 2-mercapto-5-amino-1,3,4-thiadiazole (1.500 g; 0.011 mol) in EtOH (10 ml), a solution of 4-(dimethylamino)benzaldehyde (1.640 g; 0.011 mol) in EtOH(10 ml) and some drops

of CH_3COOH (glacial) was added with stirring. The orange solution was refluxed for 4 h and cooled on ice bath, the orange ppt. was formed. The product was filtered and washed with EtOH (5 ml) and Et_2O (5 ml), and dried in oven under vacuum (Yield: 75%, m.p. 225-226°C) (Scheme 2).



Scheme 2. Preparation of daptH ligand

General preparation of complexes (1-3)

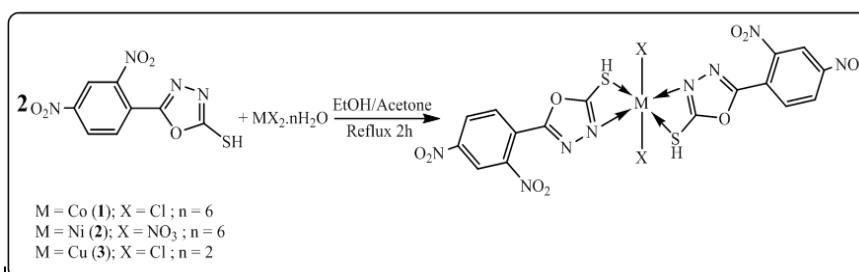
A solution of IpotH ligand (0.29 g, 1.10 mmol) in EtOH/Acetone (1:1) (15 ml) was added to (0.505 mmol) of the MX_2 (Where M = Co, Cu, X= Cl and M= Ni, X= NO_3) dissolved in distal water (10 ml). The mixture was refluxed for 2 h. The ppt. afforded was filtered off, washed with distal water, and dried in oven under vacuum.

General preparation of complexes (4-6)

A solution of daptH ligand (0.20 g, 0.074 mmol) in EtOH/Acetone (1:1) (15 ml) was added to (0.037 mmol) of the MX_2 (Where M = Co, Cu, X= Cl and M= Ni, X= NO_3) dissolved in distal water (10 ml). The mixture was refluxed for 3 h. The ppt. produced was filtered off, washed with distilledwater, and dried in oven under vacuum.

RESULTS AND DISCUSSION**Synthesis and Characterization of IpotH and its Complexes**

Reaction of two moles of IpotH ligand with one mole transition metal MX_2 (Where M = Co, Cu, X= Cl and M= Ni, X= NO_3) in distal water gave the complexes of the type $[MX_2(\kappa^2\text{-IpotH})_2]$, where M= Co (1), X = Cl; Ni (2), X= NO_3 ; Cu (3), X = Cl, (See. scheme 3). The result complexes are stable in air at room temperature, and are soluble in DMSO and DMF. but insoluble in MeOH, EtOH, acetone, $CHCl_3$ etc. The IpotH ligand has been characterized by CHN., 1H NMR., UV and IR techniques, Where as its complexes have been investigated by molar conductivity, CHNM, UV-visible, and IR techniques.



Scheme 3. Preparation of IpotH complexes(1-3)

A $10^{-3}M$ of DMSO and DMF of complexes solutions was prepared and the conductivity of at $25^\circ C$ were recorded and listed in Table 1. The values of conductivity of the prepared complexes refer that these complexes are non-electrolytes²¹.

The IpotH ligand is bonded towards the metal ions as bidentate through the N and S atoms to give octahedral arrangement around metal ions. The 1H nmr spectrum of IpotH in $DMSO-d_6$ (Fig. 1) shows a singlet peak at $\delta H = 4.401$ ppm due to the proton of thiol group, whereas the protons of phenyl ring appeared as unsolved multiplets within $\delta(6.81-7.87)$ ppm range. The peak of H-phenyl ring represents three protons, while the SH peak represents one proton, as indicated from the integration values under each signal.

IR spectrum of 2-mercapto-5-(2,4-dinitrophenyl)-1,3,4-oxadiazole (IpotH) (Fig. 2) shown a bands at (3093, 2538, 1627, 1552, 1380) cm^{-1} assigned to $\nu(C-H)$, $\nu(S-H)$, $\nu(C=N)$, $\nu(C=C)$, and $\nu(NO_2)$ respectively.

Infrared spectra of the of complexes $[MX_2(\kappa^2\text{-IpotH})_2]$ display a strong band at (1568-1594) cm^{-1} due to the $\nu(C=N)$ this bond are shifted to low frequency from that of the free ligand which appeared at (1627) cm^{-1} This indicating that IpotH ligand bounded through the nitrogen atom with metal ions 8, 17, 22. And the $\nu(S-H)$ was shifted to lower frequency compared with the free ligand.

The spectra also showed new bands at (483-508) cm^{-1} and (435-568) which due to $\nu(M-S)$ and $\nu(M-N)$ cm^{-1} respectively 8, 17, 19, 23, 24, other IR bands are listed in Table 2.

Synthesis and Characterization of $[MX_2(\kappa^2\text{-daptH})_2]$ Complexes

The refluxed two moles of daptH ligands in mixture of EtOH and acetone with one mole of transition metal MX_2 (Where M = Co, Cu, X= Cl and M= Ni, X= NO_3) in distal water gave the complexes of the type $[MX_2(\kappa^2\text{-daptH})_2]$, where M= Co (1),

X = Cl; Ni (2), X = NO₃; Cu (3), X = Cl, (See. scheme 4). All complexes are stable toward air and wetness, and obtained in high yields (over 70%), and dissolved in DMSO and DMF while partial solubility in warm

CHCl₃ and warm CH₂Cl₂. The prepared complexes have been investigated by CHNM analysis, IR spectra, conductivities measurements, and ¹H NMR for free ligand.

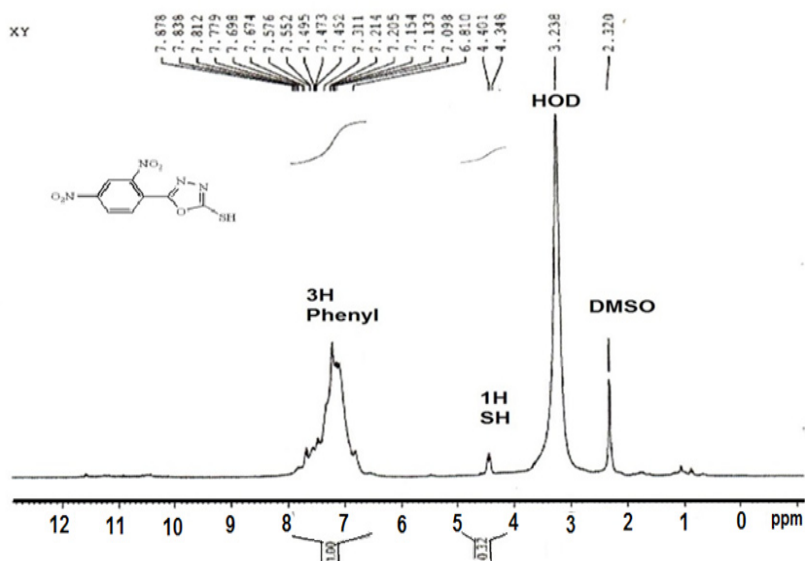


Fig. 1. ¹H NMR spectrum of lpoth measured in DMSO-d₆.

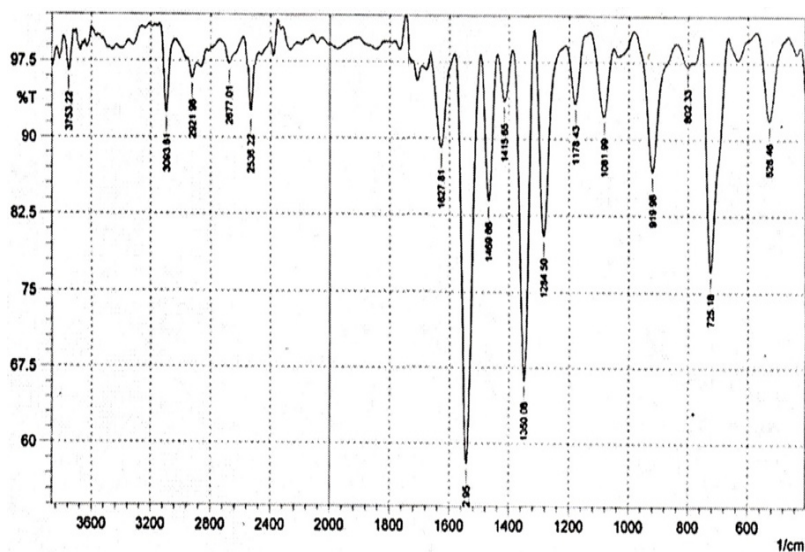


Fig. 2. IR spectrum of lpoth ligand

The molar conductance values refer to that these complexes are non-electrolytes. The daph ligand is coordinated with metal ions as bidentate through the N and S atoms to give octahedral arrangement around metal ions.

The ¹H nmr spectrum of daph in DMSO-d₆ (Fig. 3) shows a singlet peak at δ H= 3.024 ppm

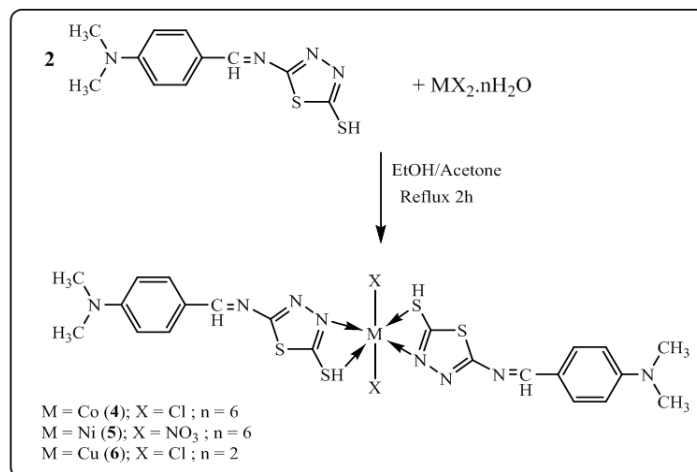
due to the proton of methyl group, and this peak represents six protons. and the proton of thiol group appeared as broad singlet at δ H= 3.792 ppm. The protons of phenyl ring appeared at δ 6.06 ppm as doublet with coupling to the neighboring protons (³JH-H= 8.40Hz) assigned to the H2,2' proton, and a doublet at δ 7.59ppm with (³JH-H= 8.40Hz) for the H1,1' proton. Whereas the protons of HC=N group appeared singlet at 8.212 ppm.

Table 1: Color, Yield, m.p., and CHNM of prepared ligands and its complexes

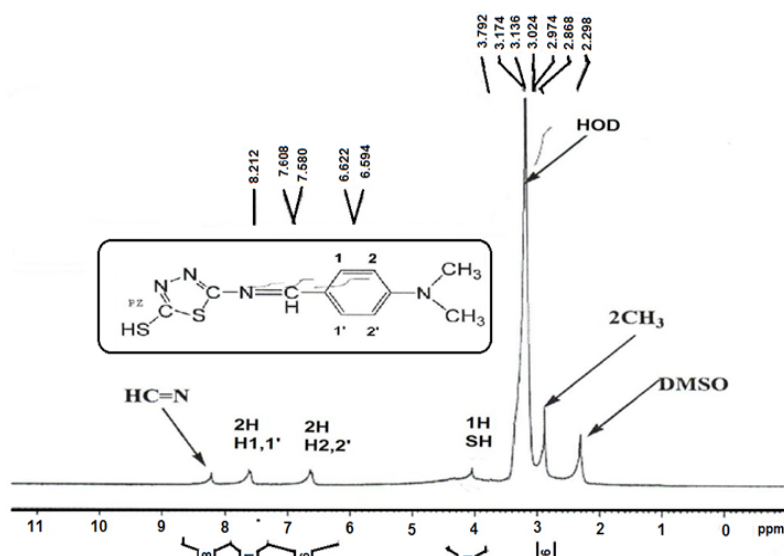
Seq.	Compounds	Color	Yield (%)	m.p. (°C)	Molar conductivity (DMSO/DMF) 10 ⁻³ M: Ω ⁻¹ mol ⁻¹ cm ⁻¹	μ _{eff} (B.M)	Elemental Analysis Found (Calc.)%	C	H	N	Metal
1	lpoth	Light yellow	74	170-173	-	-	35.67 (35.83)	1.36 (1.5)	20.69 (20.89)	-	-
2	[CoCl ₂ (κ ² -lpoth) ₂]	Light violet	79	181-185	10/19	5.1	28.67 (28.84)	1.34 (1.21)	16.57 (16.82)	8.72 (8.85)	8.72 (8.85)
3	[Ni(NO ₃) ₂ (κ ² -lpoth) ₂]	Green	86	215-218	12/18	3.1	26.89 (26.72)	1.28 (1.12)	19.65 (19.48)	8.27 (8.16)	8.27 (8.16)
4	[CuCl ₂ (κ ² -lpoth) ₂]	Brown	76	161-165	14/23	1.7	28.79 (28.65)	1.43 (1.2)	16.87 (16.7)	9.27 (9.47)	9.27 (9.47)
5	dapth	Orange	75	225-226	-	-	49.43 (49.98)	4.31 (4.58)	20.86 (21.19)	-	-
6	[CoCl ₂ (κ ² -dapth) ₂]	Dark brown	81	265-267	6/15	4.8	39.86 (40.12)	3.28 (3.67)	16.71 (17.02)	8.83 (8.95)	8.83 (8.95)
7	[Ni(NO ₃) ₂ (κ ² -dapth) ₂]	Light green	72	292-294	10/17	2.8	37.23 (37.14)	3.59 (3.4)	19.58 (19.69)	8.11 (8.25)	8.11 (8.25)
8	[CuCl ₂ (κ ² -dapth) ₂]	Green	88	253-256	15/22	1.5	39.52 (39.84)	3.24 (3.65)	16.66 (16.9)	9.45 (9.58)	9.45 (9.58)

Table 2: IR data (cm⁻¹) of the prepared ligands and their complexes

Complexes	v(C-H) _{ar}	v(C-H) _{aliph}	v(S-H)	v(C=N)	v(NO ₂)	v(M-N)	v(M-S)
lpoth	3093	-	2538	1627	1350	-	-
[CoCl ₂ (κ ² -lpoth) ₂]	3058	-	2521	1568	1371	512	443
[Ni(NO ₃) ₂ (κ ² -lpoth) ₂]	3052	-	2498	1591	1360	483	423
[CuCl ₂ (κ ² -lpoth) ₂]	3089	-	2518	1594	1360	568	508
dapth	3091	2906	2552	1650	-	-	-
[CoCl ₂ (κ ² -dapth) ₂]	3058	2889	2528	1587	-	521	438
[Ni(NO ₃) ₂ (κ ² -dapth) ₂]	3098	2923	2531	1614	-	498	421
		2858					
[CuCl ₂ (κ ² -dapth) ₂]	3052	2968	2518	1607	-	508	427
		2887					



Scheme 4. Preparation of daptH complexes (4-6)

Fig. 3. ¹H NMR spectrum of daptH measured in DMSO-d₆

IR spectrum of 2-mercapto-5-((4-(dimethylamino)benzylidene)amino)-1,3,4-thiadiazole (daptH) (Fig. 4) shown a bands at (3091, 2906, 2549, 1691, 1650, 1529, 1460) cm⁻¹ assigned to $\nu(\text{C-H})$, $\nu(\text{C-H})_{\text{aliph.}}$, $\nu(\text{S-H})$, $\nu(\text{C=N})$, $\nu(\text{C=N})$ ring, $\nu(\text{C=C})$, and $\nu(\text{C-N})$.

IR spectra of the complexes [MX₂(κ²-daptH)₂] showed a strong band at (1587-1614) cm⁻¹ due to the $\nu(\text{C=N})$ in heterocyclic ring this bond are shifted to low frequency from that of the lpotH ligand which appeared at (1650) cm⁻¹ this refer to that lpotH ligand bounded through the nitrogen atom with metal ions^{8, 17, 22}. And the $\nu(\text{S-H})$ was shifted to lower

frequency, this mean the metals ions coordinated through S atom. Other IR bands of the prepared complexes are registered in Table 2.

Electronic Spectra

The solution of the electronic measurements were prepared in using DMSO as a solvent in 10⁻³M are given in Table 3. The UV-Vis. spectra of the prepared ligands lpotH and daptH showed two bands for each ligand, at 28751 and 32258 for the lpotH and at 26385 and 32154 for the daptH which assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. The spectra for all prepared complexes are showed a similar transition as showed in the free ligands it also showed the transitions of the metal d orbitals^{21, 26}.

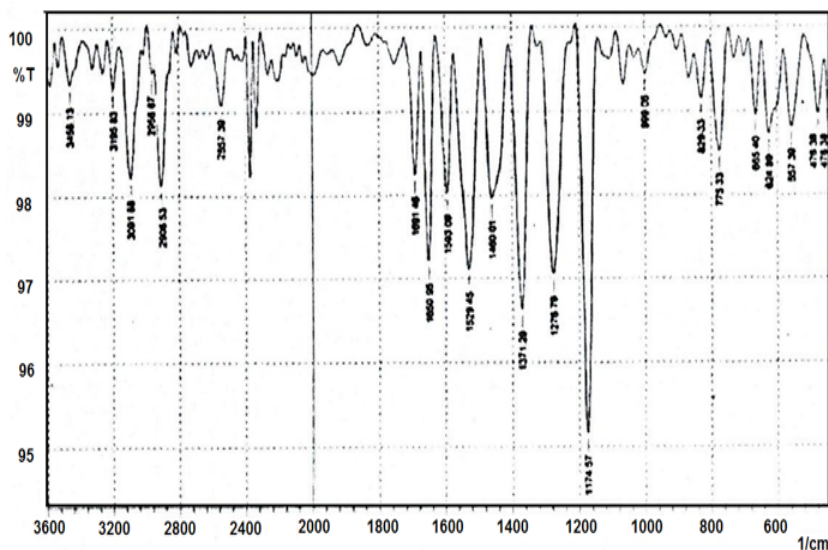


Fig. 4. IR spectrum of daptH ligand

Table 3: Electronic spectral data of prepared ligands and its complexes in DMSO

Seq.	Compounds	Absorption bands cm^{-1}	Assigned transition
1	lpotH	32258, 28751,	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
2	$[\text{CoCl}_2(\kappa^2\text{-lpotH})_2]$	30675, 27932, 9814, 10384, 18832	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^4A_2g \rightarrow {}^4T_2g(F)$, ${}^4A_2g \rightarrow 4T_1g(F)$, ${}^4A_2g \rightarrow {}^4T_1g(P)$
3	$[\text{Ni}(\text{NO}_3)_2(\kappa^2\text{-lpotH})_2]$ a	30796, 24938, 9425, 11328, 14728	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^3A_2g \rightarrow {}^3T_2g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(P)$
4	$[\text{CuCl}_2(\kappa^2\text{-lpotH})_2]$	31546, 23578, 11699	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^2Eg \rightarrow {}^3T_2g$
5	daptH	26385, 32154	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
6	$[\text{CoCl}_2(\kappa^2\text{-daptH})_2]$	33,180, 25,452 8,265, 9,346, 15,455	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^4A_2g \rightarrow {}^4T_2g(F)$, ${}^4A_2g \rightarrow {}^4T_1g(F)$, ${}^4A_2g \rightarrow {}^4T_1g(P)$
7	$[\text{Ni}(\text{NO}_3)_2(\kappa^2\text{-daptH})_2]$	30581, 24631, 9434, 10358, 13661	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^3A_2g \rightarrow {}^3T_2g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(P)$
8	$[\text{CuCl}_2(\kappa^2\text{-daptH})_2]$	29326, 22897, 11628	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, ${}^2Eg \rightarrow {}^3T_2g$

In the $[\text{CoCl}_2(\kappa^2\text{-lpotH})_2]$ spectrum, the band appeared at 9814, 10384, and 18832 cm^{-1} which due to ${}^4A_2g \rightarrow {}^4T_2g(F)$, ${}^4A_2g \rightarrow {}^4T_1g(F)$, ${}^4A_2g \rightarrow {}^4T_1g(P)$, transition respectively. The Co(II) complex showed the μ_{eff} value 5.1(B.M), indicating octahedral geometry around the center atom. Whereas in the $[\text{Ni}(\text{NO}_3)_2(\kappa^2\text{-lpotH})_2]$ spectrum, the band appeared

at 9425, 11328, and 14728 cm^{-1} which due to ${}^3A_2g \rightarrow {}^3T_2g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(F)$, ${}^3A_2g \rightarrow {}^3T_1g(P)$, transition respectively. Furthermore, octahedral geometry for Ni(II) is also supported by its magnetic moment μ_{eff} value 3.1(B.M). The other spectroscopic and physical data are in full agreements with the proposed formulations^{25,26}.

CONCLUSIONS

In summary, we have synthesized Ipoth ligand by refluxing CS₂ and 2,4-dinitrobenzohyrazide and KOH or daptH ligand by condensation of 2-mercapto-5-amino-1,3,4-thiadiazol with 4-(dimethylamino)benzaldehyde and their complexes with Co(II), Ni(II) and Cu(II) to afford mononuclear complexes of the type [MX₂(κ²-thione)₂], (M(II) = Co,

Ni and Cu). The thione ligand bonded as bidentate chelating through the nitrogen and sulfur atoms to give octahedral geometry around the metal ions with 1:2 (metal: ligand) stoichiometry. The prepared ligands and its complexes were characterization by CHNM analysis, IR spectroscopy, molar conductivity, magnetic susceptibility, UV-Visible and ¹H NMR data

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