

Synthesis and Identification of metal complexes of 1-phenyl-3-(2-(5-phenyl amino)-1,3,4-thiadiazole-2-yl) phenyl thiourea.

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Abstract:

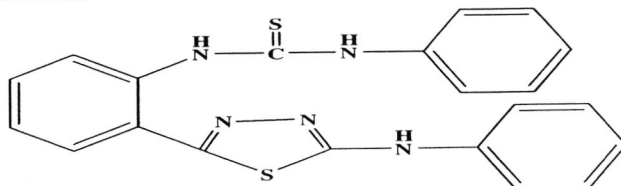
Complexes of 1-phenyl-3-(2-(5-(phenyl amino)-1,3,4-thiadiazole-2-yl)phenyl) thiourea have been prepared and characterized by elemental analysis, FT-IR, and U.V./ Visible spectra moreover, determination of metal content M% by flame atomic absorption spectroscopy, molar conductance in DMSO solution and magnetic moments (μ_{eff}).

The result showed that the ligand (L) was coordinated to Mn^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , and Hg^{+2} ions through the nitrogen atoms and sulphur atoms.

From the result obtained, the following general formula $[\text{MLCl}_2]$ has been given for the prepared complexes with an octahedral geometry around the metal ions for all complexes.

Where $\text{M} = \text{Mn}^{+2}$, Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , and Hg^{+2}

$\text{L} = 1\text{-phenyl-3-(2-(5-(phenyl amino)-1,3,4-thiadiazole-2-yl)phenyl) thiourea}$.



1-phenyl-3-(2-(5-(phenyl amino)-1,3,4-thiadiazole-2-yl) phenyl) thiourea [L]

Introduction:

The synthesis of 2,5-disubstituted-1,3,4-thiadiazole derivatives has been attracting wide spread attention due to diverse pharmacological properties such as: anti fungal [1], anti tumor [2,3], anti convulsant [4,5,6], anti inflammatory [7,8], anti bacterial [9,10,11], analgesic [8], anti ulcer [12], anti depressant and anxiolytic activities [6], therefore these compounds were used for treating several diseases [13,14,15]. They also have applications in the industry especially in the recent years [16, 17].

The later compounds have been investigated as complexing agents providing many potential binding sites for complexation in order to obtain substances with various biological activities. It was found that complexation of thiadiazole with Zn^{+2} , Cu^{+2} , Ni^{+2} , Mn^{+2} shows diuretic [18], anti bacterial and anti fungal activities [19, 20, 21]. While Cu^{+2} and Pd^{+2} complexes derived from 2, 5-disubstited thiadiazole exhibit mesomorphic properties [22]. Finally, the complexes of Ni^{+2} , Co^{+2} , Cu^{+2} and Pd^{+2} reported to use in azo-metal chelate dye [23]. Prompted by these observations, we prepare some new 2, 5-disubstituted-1, 3, 4-thiadiazole complexes with Cu^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2} .

Experimental Section:

A- Materials :

All chemicals were used without further purification.

Methyl anthranilate (Fluka) , hydrazine hydrate 40%, H_2SO_4 (BDH) , Ph NCS (Fluka) , $HgCl_2$ (BDH) , $CoCl_2.6H_2O$ (BDH) , $NiCl_2.6H_2O$ (BDH) , $CuCl_2.2H_2O$ (BDH) , $ZnCl_2$ (BDH) , $MnCl_2.4H_2O$ and $CdCl_2.H_2O$ (Fluka).

B- Instrumentation :

Melting points were recorded using electro thermal melting point apparatus. Infrared spectra were recorded with (SHIMADZU-FT-IR – 8400). The UV-Visible spectra were measured in DMSO using (SHIMADZU-UV-VIS 160A). Spectrophotometer conductivity

measurements were carried out at R.T. in DMSO using (Philips pw – digital meter).

Synthesis of the ligand [24]:

A- Preparation of N-phenyl-2-(2-(3-phenyl thioureido benzoyl) hydrazine carbothioamide (A):

A mixture of 2-aminobenzhydrazide (0.01 mole) and (0.02 mole) of phenyl isothiocyanate in ethanol absolute was heated under reflux. After (1hr) the reaction mixture was cooled and the solid product was collected and recrystallized from ethanol.

B- Preparation of 1-phenyl-3-(2-(5-(phenyl amino)-1,3,4-thiadiazole-2-yl)phenyl) thiourea (L):

(0.001 mole) of compound (A) was dissolved in (10 ml) of conc. H_2SO_4 and stirred for (1hr) then poured on to crushed ice and recrystallized from ethanol.

Synthesis of the complexes:

An ethanolic solution of metal contains (0.073 gm, 0.088 gm, 0.088 gm, 0.063 gm, 0.050 gm, 0.074 gm and 0.1 gm) or (1mmole) of $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2 \cdot H_2O$ and $HgCl_2$ respectively were added gradually with stirring to the ethanolic solution of 1-phenyl-3-(2-5-(phenyl amino)-1,3,4-thiadiazole-2-yl)phenyl) thiourea (0.2 gm) (1mmole) using stoichiometric amounts (1:1) metal : ligand molar ratios, the mixture was stirred for half an hour at room temperature, crystallized from ethanol and dried at 50 °C.

Results and Discussion:

The isolated complexes were crystallized solids in some common solvents such as DMSO and DMF. The conductivity measurements in DMSO indicated the non – electrolyte behavior, the metal determination were found to be in agreement with calculated values as in Table (1) which includes the physical properties, elemental analysis

and the magnetic measurements (μ_{eff} B.M) for these complexes. The analytical data confirmed the (1:1) (metal: ligand) composition.

Table (1): Physical properties of the complexes

Compound	Color	M.P °C	Yield	M% calculate found	$\chi_{\text{M}}(\text{cm}^3 \cdot \text{mol}^{-1})$ in DMSO 10^{-3}M	μ_{eff} (B.M)
Ligand ($\text{C}_{21}\text{H}_{17}\text{N}_5\text{S}_2$)	Yellow	240 dec.	61	-----	8.23	-----
[MnLCl ₂]	Yellow	240 dec.	70	9.32 (8.52)	9.01	5.45
[CoLCl ₂]	Brown	160 dec.	75	9.93 (9.12)	6.07	3.85
[NiLCl ₂]	Green	140	69	9.90 (8.84)	7.9	3.11
[CuLCl ₂]	Green	300 dec.	60	10.63 (9.40)	20.04	1.75
[ZnLCl ₂]	Yellow	140	76	10.90 (9.56)	7.78	D.M
[CdLCl ₂]	Yellow	280 dec.	77	17.39 (16.86)	11.66	D.M
[HgLCl ₂]	Yellow	200 dec.	80	27.30 (26.01)	7.33	D.M

Spectra studies:

Infrared spectra:

The FT-IR spectrum of the ligand (L) fig. (1) exhibited strong bands at 3398 cm^{-1} and 1662 cm^{-1} due to stretching vibration of $\nu(\text{N-H})$ and $\nu(\text{C=N})$ respectively [25,26] in addition to strong absorption band at 1228 cm^{-1} assigned to $\nu(\text{C=S})$. Complexes spectra fig. (2) showed distinct difference comparing with the spectrum of the ligand. The absorption belonging to the stretching vibration of $\nu(\text{N-H})$ have been found in the range between $(3417 - 3518) \text{ cm}^{-1}$ shifted to higher frequencies by $(19 - 120) \text{ cm}^{-1}$ [27,28] which indicates the coordination of the nitrogen atom at the (N-H) group [28], while absorption assigned for $\nu(\text{C=N})$ noticed at the range $(1612 - 1624) \text{ cm}^{-1}$ shifted to lower frequencies by $(50-.38) \text{ cm}^{-1}$ which indicates the coordination

of the ligand through the nitrogen atom at the $\nu(\text{C}=\text{N})$. The stretching vibration band $\nu(\text{C}=\text{S})$ has been found in the range $(1122 - 1083) \text{ cm}^{-1}$ shifted to lower frequency by $(106 - 145) \text{ cm}^{-1}$ which means that the sulphur atom was involved in the coordination. Metal – nitrogen and metal – sulphur band were further confirmed by the presence of the stretching vibrations of $\nu(\text{M}-\text{N})$ and $(\text{M}-\text{S})$ around $(555 - 442) \text{ cm}^{-1}$ $(401 - 451) \text{ cm}^{-1}$ respectively.

Table (2) describes the important absorption of the free ligand and its complexes.

Table (2): The infrared spectra for the free ligand and its complexes (cm^{-1})

Compounds	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	M-N	M-S
L	3398	1662	1228 875	-----	-----
[MnLCl ₂]	3417	1624	1118 752	442	412
[CoLCl ₂]	3417	1624	1122 896	540	422
[NiLCl ₂]	3456	1624	1122 756	532	401
[CuLCl ₂]	3417	1620	1122 758	547	447
[ZnLCl ₂]	3518	1612	1023 798	493	451
[CdLCl ₂]	3495	1624	1100 890	555	410
[HgLCl ₂]	3518	1620	1122 748	509	412

Electronic spectra:

The ligand (L) fig (3) exhibited absorption band in (U.V) region at wave number $(31645) \text{ cm}^{-1}$ which may be attributed to $(\pi \rightarrow \pi^*)$ transition another band of low intensity appeared at $(26809) \text{ cm}^{-1}$ is explained as $(n \rightarrow \pi^*)$ [25].

The spectra of complexes:

1. [Mn (L) Cl₂] (d^5): The spectrum of yellow complex fig (4) showed an absorption at $(32894) \text{ cm}^{-1}$ related of the charge transfer (C.T) and only one absorption band was observed in the visible region $(12106) \text{ cm}^{-1}$ which was assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (D) [29, 30]. The magnetic moment ($\mu_{\text{eff}} = 5.45 \text{ B.M}$) refer to the octahedral geometry around $\text{Mn}^{(II)}$ ion.

2. [Co (L) Cl₂] (d⁷): The spectrum of brown complex revealed the following bands at (31746) cm⁻¹ (26954) cm⁻¹, (14814) cm⁻¹ and (12738) cm⁻¹ which have been assigned to (C.T), ⁴T_{1g}→⁴T_{1g} (P), ⁴T_{1g}→⁴A_{2g} and ⁴T_{1g}→⁴T_{2g} respectively [29], the observed magnetic moment (μ_{eff} = 3.85 B.M) further illustrated the octahedral geometry around Co^(II) ion.
3. [Ni (L) Cl₂] (d⁸): The spectrum of green complex fig. (5) Displayed the following absorptions at (32051) cm⁻¹, (28985) cm⁻¹, (20408) cm⁻¹ and (12738) cm⁻¹, these bands are characteristic to the transition (C.T), ³A_{2g}→³T_{1g}(P), ³A_{2g}→³T_{1g} and ³A_{2g}→³T_{2g} respectively [30] related to octahedral Nickel (II) complex (μ_{eff} = 3.11 B.M). V₁
4. [Cu (L) Cl₂] (d⁹): The green complex of Cu (II) gave one band at (31847) cm⁻¹ caused by (C.T) transition and only one absorption band was observed at (16806) cm⁻¹ due to (²E_g→²T_{2g}) transition, the magnetic moment (μ_{eff} = 1.75 B.M) gives another evidence for the octahedral geometry around Cu (II) ion.

The yellow complexes [ZnLCl₂], [CdLCl₂] and [HgLCl₂] in which the electronic configuration of metal is (d¹⁰) confirm the absence of any (d→d) transition (31). It was found that these complexes are diamagnetic.

Table (3) reported the free ligand (L) bands of maximum absorptions and assignments related to the ligand and its complex. According to spectral data in addition of the data obtained from the metal analysis, the structural formula of the complex may be suggested as octahedral for [MLCl₂] where L= 1-phenyl-3(2-(5-phenyl amino)-1,3,4-thiadiazole-2-yl)phenyl thiourea.

M²⁺ = Mn, Co, Ni, Cu, Zn, Cd and Hg.

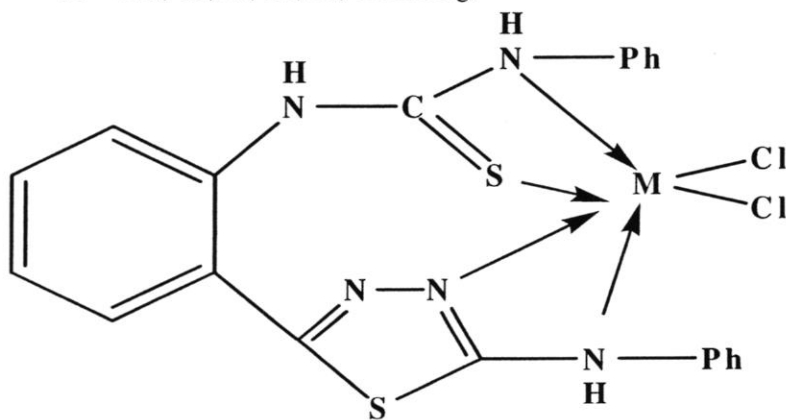


Table (3): Electronic spectra for ligand and its complexes

Complexes	λ nm	Wave number cm^{-1}	$\epsilon_{\text{max}} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	Assigned transition
L ($\text{C}_{21}\text{H}_{17}\text{N}_5\text{S}_2$)	316 373	31645 26809	1862 1905	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Mn L Cl ₂]	304 826	32894 12106	1867 20	C.T ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g(\text{D})}$
[Co L Cl ₂]	315 371 675 785	31746 26954 14814 12738	1902 931 62 30	C.T ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g(\text{P})}$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$
[Ni L Cl ₂]	312 345 490 785	32051 28985 20408 12738	1863 750 112 12	C.T ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{P})}$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$
[Cu L Cl ₂]	314 595	31847 16806	2206 30	C.T ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
[Zn L Cl ₂]	316 369	31645 27100	2251 1823	C.T C.T
[Cd L Cl ₂]	314 370	31847 27027	2009 1927	C.T C.T
[Hg L Cl ₂]	316 373	31645 26809	2193 2004	C.T C.T

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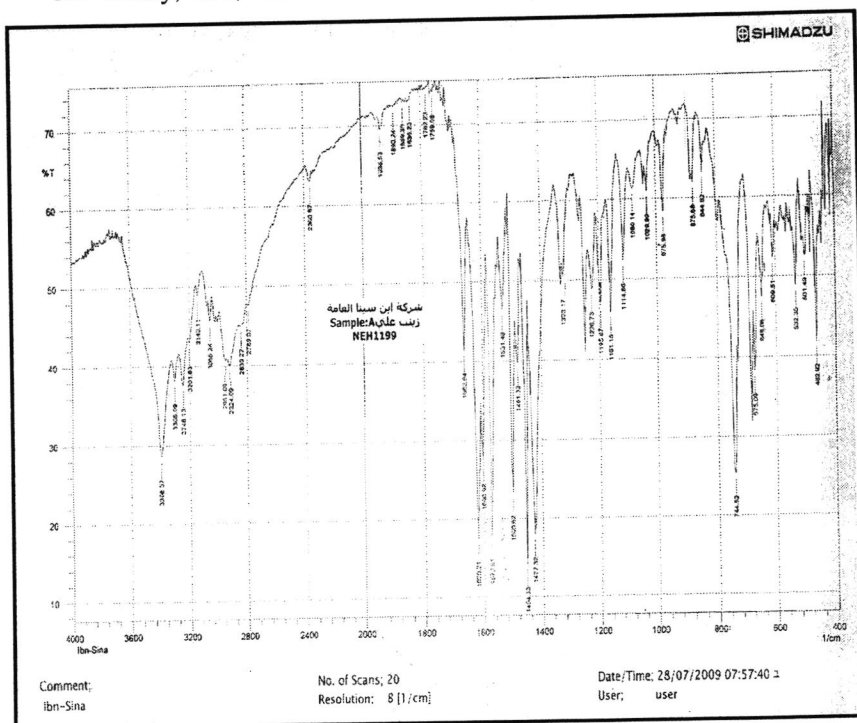
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Fig.(1): FT-IR spectrum of the ligand

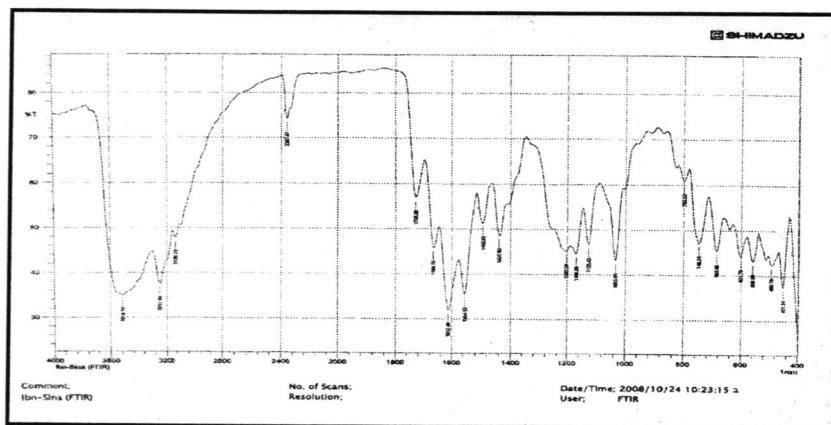


Fig.(2): FT-IR spectrum of the $[Zn L Cl_2]$ complex

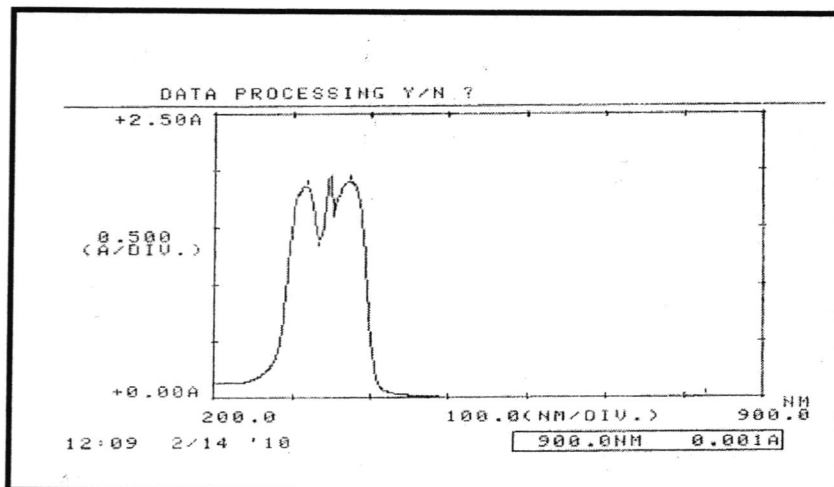


Fig.(۳): UV – Visible spectrum of the ligand

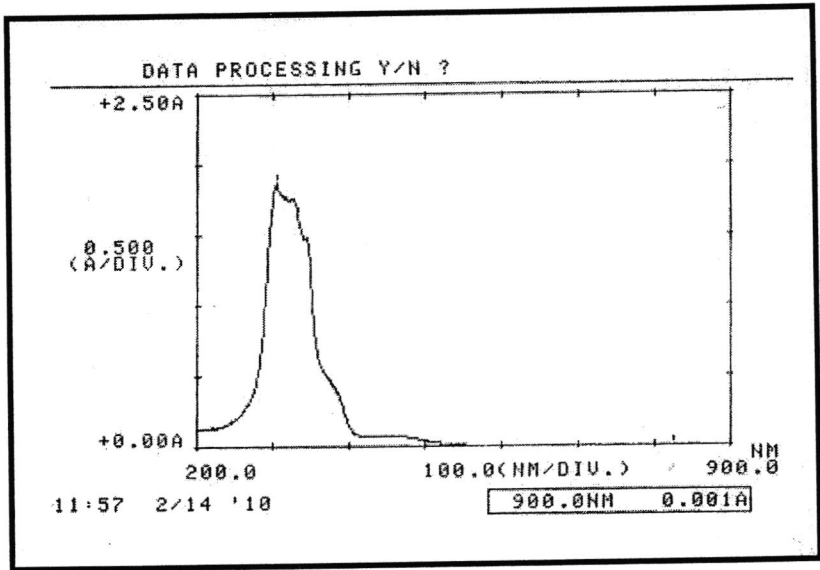


Fig (4): UV – Visible spectrum of the [Mn L Cl₂] complex

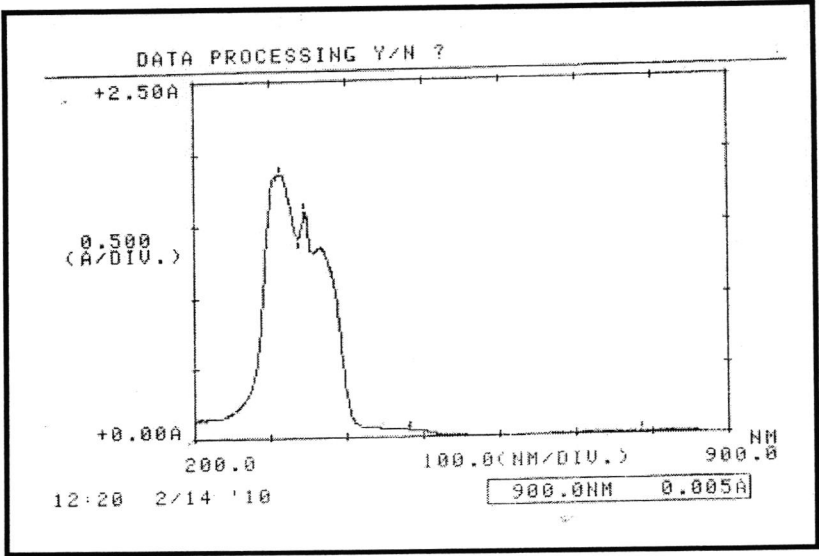


Fig (4): UV – Visible spectrum of the [Ni L Cl₂] complex