**Synthesis, characterization and spectral studies of mononuclear and binuclear Fe(II), Co (II), Ni (II), Zn(II) complexes with 2,4-dinitrophenylhydrazine dithiocarbamate**

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**Abstract:** New complexes of dithiocarbamate of the general formula [M(2,4-dinitrophenylhydra-dtc)₂], [MM'(2,4-dinitrophenylhydra-dtc)₄] where: M=Fe (II), Co(II), Ni(II),M'=Zn(II) ,2,4-dinitrophenylhydra-dtc=2,4-di nitro phenyl hydrazine dithiocarbamate and [M(1,10-phen)][M'(2,4-dinitrophenylhydra-dtc)₄], [M(1,10- phen)][M'(2,4-dinitrophenylhydra-dtc)₆] . Where: M=Co(II), Ni(II), M'=Zn(II), (1,10-phen)= 1,10-phenanthroline monohydrate. Have been prepared and characterized by atomic absorption spectroscopy infrared, conductance measurements, electronic absorption spectra, nuclear magnetic resonance and magnetic susceptibility measurements. Magnetic moments and electronic spectra indicate that the complexes of the type [M(2,-dinitrophenylhydra-dtc)₂], [MM'(2,4 -dinitrophenylhydra - dtc)₂] are of square planner geometry while the complexes of the type [M(1,10-phen)][M'(2,4-dinitrophenylhydra-dtc)₄] and [M(1,10 phen)][M'(2,4-dinitrophenylhydra-dtc)₆] have octahedral geometry.

**Keywords:** Dithiocarbamate, Iron(II), Cobalt(II), Nickel(II), Zinc(II), Complexes.

**1. Introduction**

Dithiocarbamtes are valuable compounds due to their interesting chemistry and wide utilities and application, one of the most interesting aspects of dithiocarbamtes is their applications in coordination chemistry [1,2]. Most of aliphatic and aromatic dithiocarbamate synthesized until now may coordinate only through the dithio-group behaving as unig negative bidentate ligands in reactions with metal ions [3,4].

Dithiocarbamte complexes continue to attract attention due to their ability to stabilize transition metals in a variety of oxidation states and a developing interest in this area in the functionalization of the dithiocarbamate substituent [5,6].

Transition metal dithiocarbamate complexes find use in diverse application such as material science, medicine , agriculture [7] and possess interesting structural chemistry [8-10] that make their study continuously attractive and biological activity as antibacterial, cytostatic, antifungal and immunoregulatory most of these application are based on complexation properties of dithiocarbamate ligands with metal ions specially with transition metal ions [11,12].

In view of these interesting results , we have prepared a new dithiocarbamate ligand and its complexes with different metal ions and their nitrogenous adduct.

A number of dithiocarbamate adducts have been reported in literature [13] with various geometries such as square planar [14] octahedral [15].
2. Experimental
Materials and Methods
All chemicals used in the present work were of analytical reagent (A.R) grade (B.D.H or fluka) chemical companies. Infrared spectra were recorded on Brucker 27. Alpha, A.T.R-diamond, lazer spectrophotometer in the 400- 4000 cm$^{-1}$ range without using KBr discs. Conductivity measurements were carried out on a 10$^{-3}$M solution of the complexes in DMF using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectral were recorded on a Shimadzu Uv-visible spectra photometer uv-1650 pc for 10$^{-3}$M solution of complexes in DMF as solvent at 28$^{c}$. Melting points were determined using 3000 atomic absorption. Metal content were determined using 3000 atomic absorption. Melting points were recorded on an electro thermal 9300 apparatus. The magnetic measurement was carried out at 28$^{c}$ on the solids by Sherwood scientific instrument.

Synthesis of sodium 2,4- dinitrophenyl hydrazine dithiocarbamate[6,16-18].
Aqueous solution of (4.0 gm, 0.1 mol) of sodium hydroxide was added to ethanolic solution of (19.8gm, 0.1mol) of 2,4- dinitrophenyl hydrazine with stirring. The mixture was cooled in an ice bath to this mixture (7.60 cm$^{3}$, 0.1mol) of carbon disulfide was added drop wise with continues stirring for 30 min in ice bath. The precipitate formed was extracted with (100ml) diethyl ether, filtered off washed with diethyl ether and dried under vacuum. a yellow precipitate formed

A: synthesis of complex [M(2,4- dinitrphenhydra-dtc)$_{2}$] where :
M=Fe (II), Co(II), Ni(II) of FeSO$_{4}$.7H$_{2}$O (0.278gm, 0.001 mol) or Co(NO$_{3}$)$_{2}$.6H$_{2}$O (0.291 gm, 0.001 mol) or Ni(NO$_{3}$)$_{2}$.6H$_{2}$O (80:20%) Acetone – water solution 0.291gm, 0.001 mol ) was added drop wise to ethanolic solution of sodium 2,4- dinitro phenyl hydrazine dithiocarbamate (0.592 gm, 0.002 mol) with stirring for 30 min until complete precipitation. The precipitate was filtered off washed with ethanol then with diethyl ether and dried under vacuum.

B: synthesis of complex [MM`(2,4-dinitrphenhydra-dtc)$_{4}$] where :
M=Fe (II), Co(II), Ni(II), M`=Zn(II)
Aqueous solution of ZnSO$_{4}$.7H$_{2}$O (0.2875 gm, 0.001 mol) was added drop wise with continuous stirring to ethanolic solution of sodium 2,4- dinitro phenyl hydrazine dithiocarbamate (1.184gm,0.004mol) to form Na$_{2}$[Zn(2,4- dinitrphenhydra-dtc)$_{4}$]. 80:20% acetone- water solution of FeSO$_{4}$.7H$_{2}$O (0.278gm, 0.001 mol) or Co(NO$_{3}$)$_{2}$.6H$_{2}$O (0.291 gm , 0.001 mol) or Ni(NO$_{3}$)$_{2}$.6H$_{2}$O (0.291 gm, 0.001 mol)was added drop wise with continuous stirring for 30 min until complete precipitation. The precipitate was filtered off washed with ethanol then with diethyl ether and dried under vacuum.

C: synthesis of complex [M(1,10- phen)$_{3}$][M`(2,4-dinitrphenhydra-dtc)$_{4}$] where :
M=Co(II), Ni(II), M`=Zn(II)
Prepared by adding mixture of Co(NO$_{3}$)$_{2}$.6H$_{2}$O (0.29gm, 0.001 mol) and 1,10 phenanthroline (0.7035gm,0.003 mol) or adding mixture of Ni(NO$_{3}$)$_{2}$.6H$_{2}$O (0.29gm, 0.001 mol) and 1, 10 phenanthroline(0.7035 gm, 0.003 mol) which dissolved in 80:20 % acetone- water added to Na$_{2}$[Zn(2,4- dinitrphenhydra-dtc)$_{4}$] (1.2035 gm, 0.001 mol) which prepared in 1:B with continuous stirring for 30 min the mixture was leaved for 3 days until complete precipitation. The precipitate formed was filtered washed with acetone then dried under vacuum.

D: synthesis of complex [M(1,10- phen)$_{3}$][M`$^{3}$(2,4- dinitrphenhydra-dtc)$_{6}$] Where:
M=Co(II), Ni(II), M`=Zn(II)
Prepared by adding a mixture of Co(NO$_3$)$_2$.6H$_2$O (0.29gm, 0.001 mol) and 1,10 phenanthroline monohydrate (0.7035gm , 0.003 mol) or adding mixture of Ni(NO$_3$)$_2$.6H$_2$O (0.29gm, 0.001 mol) and 1,10 phenanthroline monohydrate (0.7035gm , 0.003 mol) which dissolved in 80:20% acetone-water solution to a mixture of Na$_2$[Zn$_2$(2,4-dinitrphenhydra-dtc)$_6$] which prepared of dissolving ZnSO$_4$.7H$_2$O(0.5750gm , 0.002mol) and sodium 2,4–dinitro phenyl hydrazine dithiocarbamate (1.776 gm , 0.006 mol) drop wise with continuous stirring for 30 min, the precipitate formed was filtered, washed with acetone then dried under vacuum.

3. Results and discussion

The new ligand was prepared by the reaction of 2,4- dinitro phenyl hydrazine with sodium hydroxide and then added carbon disulphide. The complexes were prepared through direct reaction of the FeSO$_4$.7H$_2$O or Co(NO$_3$)$_2$.6H$_2$O or Ni(NO$_3$)$_2$.6H2O with the above ligand in (1:2) molar ratio, other complexes were prepared through direct reaction of the ZnSO$_4$.7H$_2$O with the FeSO$_4$.7H$_2$O or Co(NO$_3$)$_2$.6H$_2$O or Ni(NO$_3$)$_2$.6H$_2$O with the above ligand.

The values of conductivity in dimethylformamide solution of the complexes ranged from (0.70$\rightarrow$12.5) cm$^2$ ohm$^{-1}$ mol$^{-1}$ for the complex [M(2,4- dinitrphenhydra-dtc)$_2$] and complex [MM`(2,4-dinitrphenhydra-dtc)$_4$] which are typical values for nonelectrolyte type [19]. While the values of conductivity of the complexes [M(1,10- phen)$_3$][M`(2,4-dinitrphenhydra-dtc)$_4$] [M(1,10- phen)$_3$][M`,2(2,4- dinitrphenhydra-dtc)$_6$] ranges from (74.4$\rightarrow$84.3) cm$^2$. ohm$^{-1}$. mol$^{-1}$ which are typical for electrolyte type as shown in table (1) [20].

3.1. Magnetic Susceptibility Measurements

The magnetic moments of the complexes were measured at 28 C°. The magnetic moments for Fe(II) , Co(II) and Ni(II) complexes (1$\rightarrow$6) were (1.83$\rightarrow$5.04) B.M. suggesting a square planner geometry as shown in table(1) [20].

The low value of magnetic moment for complex (5) is due to antiferromagnetic interaction. The magnetic moments of other complexes (7$\rightarrow$10) were in the range (2.69$\rightarrow$4.62) B.M in an octahedral geometry as shown in table (1) [21].

3.2. Infrared Spectral Studies

The important IR bands of the ligand and its complexes are listed in table (2). The stretching frequency of the v (C---N) band for the dithiocarbamate was intermediate between the stretching frequencies associated with typical single and double-bonded carbon and nitrogen atoms [21]. The v (C----N) and v (C---S) of complex type [M(2,4-dinitrphenhydra-dtc)$_2$] and [MM'(2,4-dinitrphenhydra-dtc)$_4$] were observed in the range of (1513-1603)cm$^{-1}$ and (1046-1077)cm$^{-1}$. The presence of only one band in the later region reports the bidentate coordination of the dithio ligand [22-25]. IR spectra of the complex type [M(2,4-dinitrphenhydra-dtc)$_2$] and [MM'(2,4-dinitrphenhydra-dtc)$_4$] showed a new band at (407- 471) cm$^{-1}$ which are evidence for the coordination of metal to sulfur v (M-S) this behavior may be attributed to electron releasing of the amines which forces high electron density towards the sulfur atoms as shown in table (2).

Also the v (M'- S) was observed in the range (401-414) cm$^{-1}$ for complex type [MM'(2,4-dinitrphenhydra-dtc)$_4$]. The IR spectra of complex type [M(1,10 phen)$_3$]M'(2,4-dinitrphenhydra-dtc)$_4$ and [M(1,10- phen)$_3$]M`(2,4- dinitrphenhydra-dtc)$_6$ showed one band at (415-470) cm$^{-1}$ which are evidence for the coordination of metal to sulfur v (M'-S). in addition to the v (M-N) was observed in the range(486-649) region [26] in the adduct as shown in table (2).
Table 1. Analytical and some physical properties of the prepared complexes.

| No | Compound | Color        | M.P. | Molar conductivity | %M   | % yield | μ eff | B.M. |
|----|----------|--------------|------|--------------------|------|---------|-------|------|
|    | C7H5N4O4S2Na | light yellow | 276  | –                  | –    | 83.4    | –     | –    |
| 1. | [Fe(2,4-Dinitrphenhydra-dtc)] | Light Yellow | 310  | 11.76              | 8.363| 91.66   | 5.04  |
| 2. | [Co(2,4-Dinitrphenhydra-dtc)] | Light Brown  | 290  | 8.70               | 8.96 | 90      | 4.16  |
| 3. | [Ni(2,4-Dinitrphenhydra-dtc)] | Dark Brown   | 300  | 0.70               | 9.35 | 93.46   | Diam  |
| 4. | [FeZn(2,4-Dinitrphenhydra-dtc)] | Light Yellow | 254  | 9.38               | 4.24 | 61.85   | 3.51  |
| 5. | [CoZn(2,4-Dinitrphenhydra-dtc)] | Light Yellow | 256  | 12.5               | 4.46 | 52.67   | 1.83  |
| 6. | [NiZn(2,4-Dinitrphenhydra-dtc)] | Dark Yellow  | 285  | 10.6               | 4.22 | 53.08   | Diam  |
| 7. | [Co(1,10-phen)]²[Zn(2,4-Dinitrphenhydra-dtc)]² | Dark Yellow | 248  | 74.4               | 2.76 | 60.94   | 4.60  |
| 8. | [Ni(1,10-phen)]²[Zn(2,4-Dinitrphenhydra-dtc)]² | Light Yellow | 260  | 78.8               | 2.64 | 5730    | 3.41  |
| 9. | [Co(1,10-phen)]²[Zn²(2,4-Dinitrphenhydra-dtc)]² | Brown       | 190  | 82.7               | 2.04 | 70.27   | 2.69  |
| 10. | [Ni(1,10-phen)]²[Zn²(2,4-Dinitrphenhydra-dtc)]² | Dark Brown  | 200  | 84.3               | 2.08 | 60.47   | 3.17  |

3.3. Electronic Spectral Studies

The UV-visible spectra of the ligand and its complexes of 10⁻³ M solution in DMF were recorded. The results were listed in table(2). The UV-visible spectrum of the Fe(II) complex (1) gives absorption bands at (21692) cm⁻¹, (32258) cm⁻¹ regions. The UV-visible of Fe(II) complex(4) gives absorption bands at (21978) cm⁻¹ and (33003) cm⁻¹ regions which corresponds to (d-d) transition in square planer geometry as shown in table (2) [5, 27, 28].

The Co(II) complex (2) exhibited an absorption band at (21505 cm⁻¹) regions which was assigned (¹A₁g → ³Eg) transition and the Co (II) complex(5) exhibited an absorption band at (22371 cm⁻¹) regions which was assigned to (¹A₁g → ³Eg) transition [29]. The Ni(II) complex (3) exhibited an absorption band at (27855 cm⁻¹) which was assigned to (¹A₁g → ³B₁g) transition in square planar geometry.
The Ni(II)complex (6) show two absorption bands at (22124 cm\(^{-1}\)) and (32753 cm\(^{-1}\)) which were assigned to \((^1A_g \rightarrow ^1B_2g)\) and \((^1A_g \rightarrow ^1B_1g)\) transitions in square planar geometry [30]. The complex (7) show an absorption band at (31153 cm\(^{-1}\)) region and the complex(9) show an absorption band at (23041 cm\(^{-1}\)) region which were assigned to \((^4T_1g(F) \rightarrow ^4T_1g (P))\) transition in an octahedral geometry of high spin [31-33].

The complex(8) show an absorption band at (34014 cm\(^{-1}\)) region which was assigned to \((^4A_2g(F) \rightarrow ^4T_1g (P))\) transition and the complex(10) show two absorption bands at (22573 cm\(^{-1}\)) and (32501 cm\(^{-1}\)) region which were assigned to \((^4A_2g(F) \rightarrow ^3T_1g (F))\) and \((^4A_2g(F) \rightarrow ^3T_1g (P))\) transition in octahedral configuration as shown in table (2) [34].

| No | Compound | U.V band (\(\text{cm}^{-1}\)) | \(\nu (\text{C}-\text{N})\) | \(\nu (\text{C}-\text{S})\) | \(\nu (\text{M}-\text{S})\) | \(\nu (\text{M'}-\text{S})\) | \(\nu (\text{M}-\text{N})\) |
|----|-----------|-------------------------------|----------------|----------------|----------------|----------------|----------------|
|    | C7H5N4O4S2Na | 21.000 32.000 | 1512 | 1093 | - | - | - |
| 1. | [Fe(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 21.692 32259 | 1516 | 1046 | 407 | - | - |
| 2. | [Co(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 21505 | 1513 | 1051 | 411 | - | - |
| 3. | [Ni(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 27855 | 1516 | 1077 | 403 | - | - |
| 4. | [FeZn(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 21978 33003 | 1603 | 1043 | 460 | 401 | - |
| 5. | [CoZn(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 22371 31153 | 1600 | 1059 | 462 | 413 | - |
| 6. | [NiZn(2,4- Dinitrphenydra-dtc)]\text{$_2$} | 22124 32573 | 1513 | 1058 | 471 | 414 | - |
| 7. | [Co(1,10- phen)$_3$]$^2$[Zn(2,4- Dinitrphenydra-dtc)]$^2$ | 31153 | 1465 | 1116 | - | 470 | 510 |
| 8. | [Ni(1,10- phen)$_3$]$^2$[Zn(2,4- Dinitrphenydra-dtc)]$^2$ | 34014 | 1453 | 1114 | - | 415 | 649 |
| 9. | [Co(1,10- phen)$_3$]$^2$[Zn(2,4- Dinitrphenydra-dtc)]$^2$ | 23041 | 1455 | 1115 | - | 419 | 486 |
| 10. | [Ni(1,10- phen)$_3$]$^2$[Zn(2,4- Dinitrphenydra-dtc)]$^2$ | 22573 32051 | 1457 | 1114 | - | 430 | 505 |
3.4. The $^1$H-NMR, Spectra for the Ligand $L$

$^1$H-NMR study of the ligand = 2,4- dinitrophenyl hydrazine dithiocarbmate. The first peak was strong and observed in the region 2.45 because it was far from each of electron withdrawing groups which was agree with appeared theoretical measurements for the compound, in the in region 2.0 , (2) while the second peak has been showed in the region 4-2 in the N.M.R measurements, confirmed by the theoretical measurement of compound in the position 4.0 while the broad peak appeared around 9.1 -7.5 belonging to benzene cycle confirmed by the theoretical measurements and the interpretation of photons which connected with benzene cycle appeared as follow as. H5 appeared in the position, 8.97 because it is near from two withdrawing groups and it is confirmed by the theoretical measurement. H4 the other peak has been appeared in the region 8.2 because it is adjacent to one group of NO$_2$ and it is agree with the theoretical measurements 8.57.

The other peak in the region 7.5-7 belonging to the H3 and it is confirmed by approximately the theoretical and agree with and confirmed by published researches as shown in figure (1) [35-39].

4. Conclusion

In this work, the synthesis and characterization ligand and their complexes. Physicochemical and spectroscopic methods have been put in place to verify bonding mode and over all complex structure. From These measurement results lead to the preparation of ten coordinate complexes and from above discussions the structure of complexes has been suggested which is complexes (1→6) a square planar geometry and other complexes (7→10) were an octahedral geometry as shown in figure (2-5).
ChemNMR $^1$H Estimation

Estimation quality is indicated by color: good, medium, rough
**Figure 1(a,b,c).** $^1$H- NMR of the ligand Sodium -2,4- dinitrophenylhydrazine dithiocarbamate
(b)
Figure 2. Suggest structures (a): complexes[1,2,3] (b): complexes[4,5,6] (c):complexes[7,8] (d): complexes [9,10].
Figure 3. Suggest structure of complex (5)

Figure 4. Suggest structure of complex (5) by molecular mechanic
Figure 5. Suggest structure complex (1) by molecular mechanic

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