

# Preparation, Characterization and Structural Determination of some Coordination Compounds of Quadridentate Thiosemicarbazone

Abdelraziq E. Hamedelniel, Ragab R. Amin\* and Iman Shedaiwa

Chemistry Department, Faculty of Science

Sana'a University, P.O. Box 1247, Sana'a – Yemen

\*E-mail: ragab@rramin.net

## تحضير وتمييز الأشكال التركيبية لمركبات ثيوسيميكاربازون رباعية الارتباط

عبد الرزاق الفكي حمد النيل ورجب رياض أمين وإيمان محمد شديدة  
قسم الكيمياء كلية العلوم جامعة صنعاء - صنعاء ص . ب . ١٢٤٧ الجمهورية اليمنية

تم تحضير ودراسة خواص مجموعة جديدة من مترابكات الأيونات الثنائية لعناصر الكوبلت والنيكل والنحاس مع مشتقات كل من بنزل مضاعف (٤-باراكلوروفينيل ثيو سيمبكاربازون) وبنزل مضاعف (٤-بارابروموفينيل ثيوسيميكاربازون). تم فصل المترابكات ودراسة الأشكال الكيميائية الفراغية المناسبة لها بناء على نتائج التحليل الكمي الميكروني للعناصر ودراسة التحليل الطيفي في مجال الأشعة تحت الحمراء وطيف الانتقال الإمتصاصي الإلكتروني لمحاليل المترابكات والقياسات المغناطيسية ودراسة نتائج التحليل الحراري للمواد الصلبة. أثبتت نتائج الدراسات أن المرتبطات قيد الدراسة تتعامل مع أيونات الفلزات الثنائية كمرتبط يحمل شحنتين سالبتين رباعي الارتباط مكوناً مترابكات من خلال مواقع ذرات النيتروجين والكبريت والكبريت والنيتروجين (NSSN) ولها الصيغة الجزيئية  $ML$  and  $ML \cdot 2H_2O$  أوضحت النتائج من خلال القياسات الطيفية والمغناطيسية أن مترابكات الكوبلت والنيكل تتفق تماماً مع المترابكات ثمانية الأوجه المعروفة.

**Keywords:** *Metal Complexes, Thiosemicarbazone*

### ABSTRACT

New transition metal complexes of  $Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$  with benzil bis 4-(p-Chlorophenyl-thiosemicarbazone) and benzil bis 4-(p-Bromophenyl-thiosemicarbazone) were synthesized. Attempts were made to ascertain their probable structures on the basis of elemental analysis, infrared and electronic spectra, thermal and magnetic studies. Ligands can function as a bidentate quadridentate with the metal ions forming complexes in a molar ratio 1:1 having the formula ( $ML$  and  $ML \cdot 2H_2O$ ). The magnetic moment measurements and the crystal field parameters calculated for  $Co^{II}$  and  $Ni^{II}$  complexes agree well with that reported for known octahedral complexes.

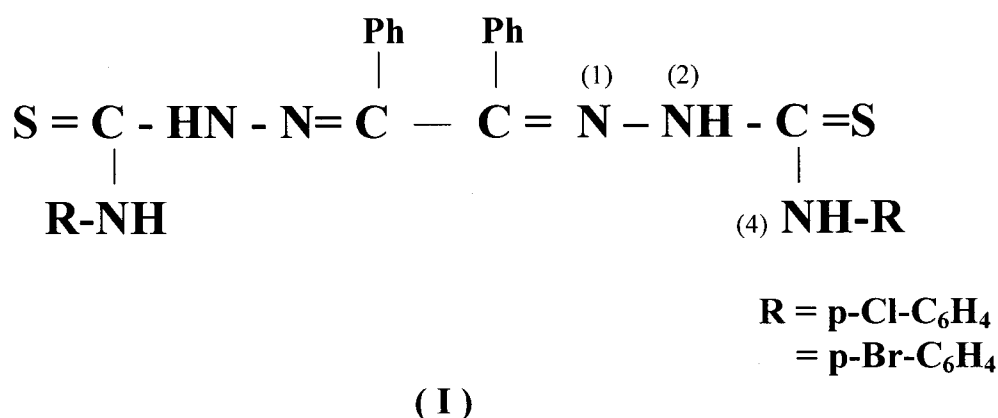
## 1. Introduction

Thiosemicarbazones are of current interest with respect to their biological activity and chemotherapeutic properties [1-5]. In addition, these compounds have many applications especially as reagents for the microanalytical determination as well as their ability to form chelate complexes with transition metal ions [6-13]. This paper investigates the chelating properties of Benzil-bis(4-p-chlorophenyl-thiosemi-carbazone), H<sub>2</sub>CTS and Benzil-bis(4-p-Bromophenyl-thiosemi-carbazone), H<sub>2</sub>BTS with cobalt (II), nickel(II) and copper (II) ions. Elemental analyses, different spectroscopic techniques, magnetic measurements and thermal analyses were used to elucidate both stoichiometry and structures of these isolated compounds.

## 2. Experimental

The chelating agents, H<sub>2</sub>CTS, and H<sub>2</sub>BTS, were prepared by mixing an ethanolic solution of benzil (0.1 mmole) and 4-p-chlorophenyl thiosemicarbazide (0.2 mmole) or 4-p-Bromophenylthiosemicarbazide in the same solvent. The reaction mixture was held under reflux in a water bath for 1.5 hrs, where few drops of glacial acetic acid were added in the beginning of reflux. The yellow precipitate thus formed was filtered off, recrystallized from absolute ethanol and dried in a desiccator over silica gel, (Yield 85%). H<sub>2</sub>CTS and H<sub>2</sub>BTS were identified with elemental analysis and I.R spectra (structure I).

The complexes were prepared by adding an ethanol solutions of equimolar amounts of H<sub>2</sub>CTS and metal (II) salt. The mixtures were heated on a water bath for 2 hrs and allowed to evaporate slowly prior to filtration. The precipitates were washed with hot ethanol and dried with diethyl ether and preserved in a desiccator over silica gel. Yield 60-80%.



Structure I

**Table 1:** Analytical Results for the Complexes of Benzil bis 4-p-Bromophenyl thiosemicarbazone Derivative

Compound	Colour	$\mu_B$	% C calc.(found)	%H (3.0)	%Metal oxide (10.1)	$\Delta E$ Kcal/mol
$C_{28}H_{22}N_6S_2Br_2$	Yellow	-	50.40 (50.9)	3.3 (3.0)	- (10.1)	10.6
[Cu(L)]	Dark brown	1.2	46.8 (46.9)	2.8 (3.1)	11.1 (11.4)	15.8
[CoL.2H <sub>2</sub> O]	Dark red	1.8	44.15 (44.5)	3.2 (3.5)	9.8 (10.2)	14.8
[NiL.2H <sub>2</sub> O]	Dark green	2.21	44.2 (44.4)	3.2 (3.3)	9.9 (10.1)	15.6

### 3. Results and Discussion

#### IR spectral studies

The elemental analyses are consistent with 1:1 metal to ligand stoichiometry for all isolated complexes as shown in table 1. The complexes are quite stable in air and soluble in most organic solvents. The infrared spectra of the free ligands, H<sub>2</sub>CTS and H<sub>2</sub>BTS, exhibit absorption bands at 3196cm<sup>-1</sup> and 3245cm<sup>-1</sup> assigned to  $\nu$  [N<sup>2</sup>H] and  $\nu$  [N<sup>4</sup>H], respectively [14]. The thioamide group, (NH-C=S), gives rise to bands I-IV at 1534, 1325, 980 and 786cm<sup>-1</sup>. The strong band at 1534cm<sup>-1</sup> in the infrared spectra of the free ligands is assigned to the combination of  $\nu$  (C=N) and  $\nu$  (C=C) modes [15]. The bands around 1325 and 786cm<sup>-1</sup> observed in the free ligands may be assigned to  $\nu$  (C=S) vibration [8]. However, the cobalt (II), nickel (II) and copper (II) complexes lack any absorption due to  $\nu$  (C=S) and  $\nu$  [N<sup>2</sup>H], which implies deprotonation of the bis-thiosemicarbazones on coordination [15].

The disappearance of  $\nu$  [N<sup>2</sup>H] and  $\nu$  (C = S) with the simultaneous appearance of new bands in the 1550-1560cm<sup>-1</sup> region, and a weak new bands at 610-615cm<sup>-1</sup> which are attributed to  $\nu$  (C = N) and  $\nu$  (C

**Table 2:** The crystal field splitting energies,  $\Delta_o$  and some electronic ligand field parameters for Co(II) and Ni(II) complexes of Benzil bis 4-p-Bromophenyl thiosemicarbazone and Benzil bis 4-p-Chlorophenyl thiosemicarbazone Derivatives.

Complex	$\Delta_o$ , (KJ/mol)	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_2/\nu_1$	B (cm <sup>-1</sup> )	$\beta$
[Co(CTS).2H <sub>2</sub> O]	417.6	11,300	23,900	30,600	2.11	1016	1.1
[Ni(CTS).2H <sub>2</sub> O]	408.1	14,300	25,700	32,100	1.77	920	0.86
[Co(BTS).2H <sub>2</sub> O]	403.2	12,100	24,800	30,100	2.05	1090	1.1
[Ni(BTS).2H <sub>2</sub> O]	398.2	9,900	13,500	24,200	1.36	988	0.88

= S) [16], respectively, indicates the involvement of the nitrogen and sulphur atoms in bonding to the metal ions through enothiolization.

The higher shifts in wave number for  $\nu(\text{N-N})$  by  $5\text{--}15\text{cm}^{-1}$  and the appearance of new bands in the low frequency region at  $434$ ,  $440$  and  $448\text{cm}^{-1}$  for the respective Ni (II), Co (II) and Cu (II) complexes due to  $(\text{M} \leftarrow \text{N})$  [14-17], confirm the participation of the azomethine nitrogen in bonding. These data may suggest structure II for the isolated complexes.

### Electronic spectra and magnetic measurements

The electronic spectra of the  $[\text{Ni}(\text{BTS})_2 \cdot 2\text{H}_2\text{O}]$  complex show two bands, at  $24200$  and  $13500\text{cm}^{-1}$  assigned to the  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\nu_3)$  and  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\nu_2)$  transition, respectively. The  $\nu_1$  position is found to be  $9900\text{cm}^{-1}$ ; thus  $\nu_2/\nu_1 = 1.36$ . The Dq, B and  $\beta$  values were calculated from the observed positions of the bands and are  $988\text{cm}^{-1}$ ,  $538.6\text{cm}^{-1}$  and  $0.88$ , respectively (Table 2). These values together with the magnetic susceptibility ( $2.3\mu_B$ ) support the octahedral structure [18].

The magnetic moment value ( $1.8\mu_B$ ) for  $[\text{Co}(\text{BTS})_2 \cdot 2\text{H}_2\text{O}]$  is near the spin only value for low-spin octahedral cobalt (II) complexes. The electronic spectrum has a strong peak around  $23800\text{cm}^{-1}$  which is due to the  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  transition [19]. The other characteristic bands for d-d transition are difficult to recognize in this complex.

The electronic spectra of the  $[\text{Ni}(\text{CTS})_2 \cdot 2\text{H}_2\text{O}]$  complex show two bands, at  $25700$  and  $14300\text{cm}^{-1}$  assigned to the  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\nu_3)$  and  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\nu_2)$  transition, respectively. The  $\nu_1$  position is found to be  $14300\text{cm}^{-1}$ ; thus  $\nu_2/\nu_1 = 1.35$ . The Dq, B and  $b$  values were calculated from the observed positions of the bands and are  $920\text{cm}^{-1}$ ,  $540\text{cm}^{-1}$  and  $0.86$  respectively. These values together with the magnetic susceptibility ( $2.45\mu_B$ ) support the octahedral structure [19].

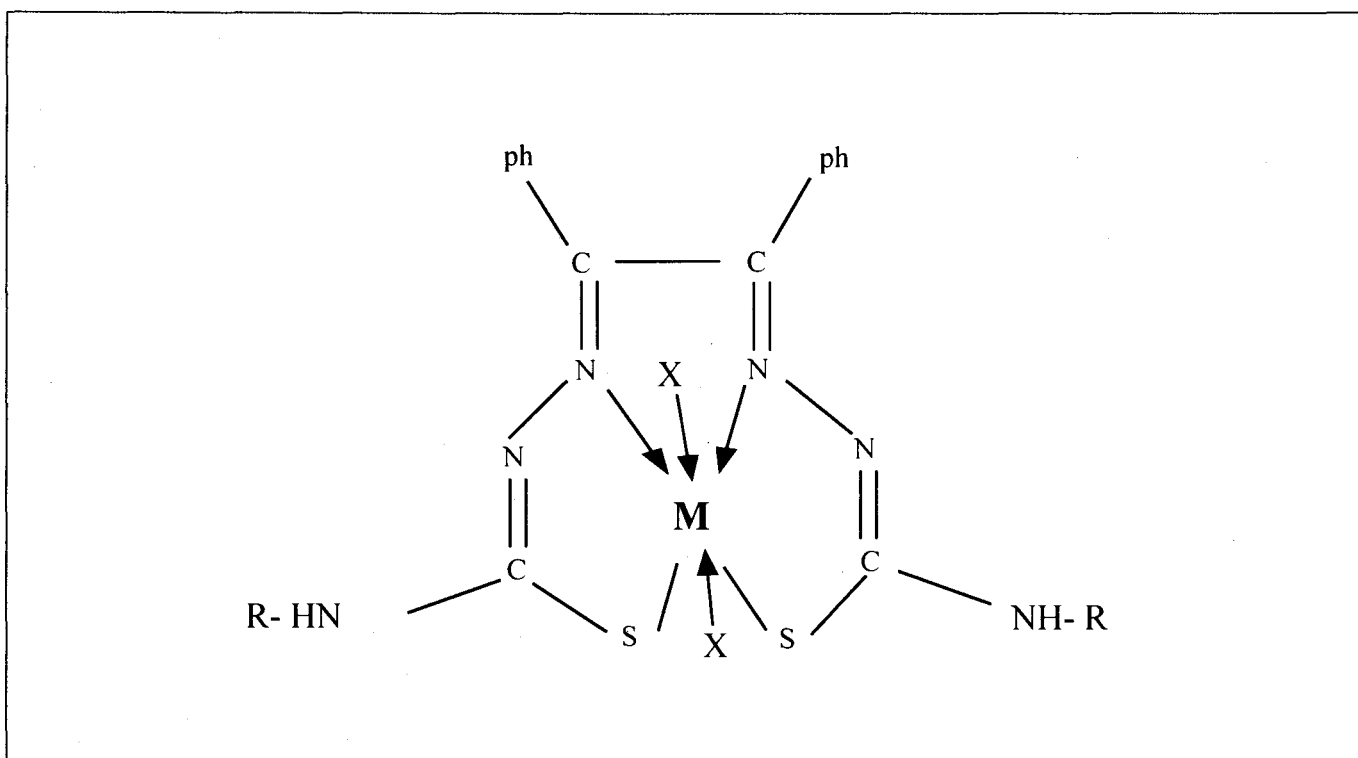
The electronic spectrum for  $[\text{Cu}(\text{BTS})]$  complex shows a good 3 d-d transition. The spectrum shows a clear shoulder at  $17500\text{cm}^{-1}$  which may be due to a combination of  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transitions in a square-planar configurations [19]. However, the strong band observed at  $26300\text{cm}^{-1}$  may be assigned as a charge-transfer, probably,  $d\text{-}\pi^*$ . Also, the broad band centered at  $20600\text{cm}^{-1}$  in the spectrum of  $[\text{Cu}(\text{BTS})]$  may be due to  $\text{Cu} \rightarrow \text{L}$  charge transfer [20]. The room temperature magnetic moment ( $1.2\mu_B$ ) for the copper (II) complex shows a subnormal magnetic moment which may arise from metal – metal interaction [21].

The crystal field splitting energies,  $\Delta_o$  in kilojoules per mole for Co(II) and Ni(II) metal complexes and their adducts can be calculated from the following relation [22]

$$\Delta_o (\text{kJ/mol}) = hc N / \lambda$$

where  $h = 6.626 \times 10^{-34}$  (J.s),  $c = 3.00 \times 10^8$  (m/s),  $\lambda$  = wavelength (m) and  $N = 6.023 \times 10^{23}$  (ions/mol).

The calculated values of the crystal field splitting energies,  $\Delta_o$ , were tabulated in Table 2. These values indicate that the degree of splitting of the  $d$  orbital is affected by the substitution in the  $p$ -position of the benzene ring following the spectrochemical series [22].



### Structure II

$M = \text{Co(II)}, \text{Ni(II)}, X = \text{H}_2\text{O}$

$= \text{Cu(II)}, X = \text{zero}$

$R = p\text{-Cl-C}_6\text{H}_4 \text{ or } p\text{-Br-C}_6\text{H}_4$

### Thermal analysis

The thermal behaviour of Ni(II), Co(II), Cu(II) complexes with  $\text{H}_2\text{BTS}$  were studied by TG and DTG. The TG thermograms of Co(II) complex, show a weight loss at  $192^\circ\text{C}$  (calc 6.42% found 6.25%) corresponding to loss of water from the coordination sphere of the complex. The anhydrous Co(II) complex begins to decompose from  $192^\circ\text{C}$  through different exothermic peaks at 247, 288, 330 and 350 up to  $600^\circ\text{C}$  which may be respectively attributed to phase change of the complex, melting point and decomposition of the organic parts with final formation of cobalt oxide at  $600^\circ\text{C}$  [23].

The TG thermograms of Ni(II) complex, show a weight loss at  $195^\circ\text{C}$  corresponding to loss of coordinated water molecules. The exothermic peak at  $280^\circ\text{C}$  is assigned to bond breaking between the metal ions and coordinated water molecules in  $[\text{Ni}(\text{BTS})_2 \cdot 2\text{H}_2\text{O}]$  complex. The broad exothermic peaks at  $370\text{-}400^\circ\text{C}$  include various processes of decomposition with the loss of the organic portion and the subsequent formation of the final NiO product. The remaining mass of NiO is in good agreement with the calculated one [24].

Thermoanalytical methods are excellent tools to follow the thermal decomposition of the ligand and complex materials. The weight percent at each temperature in TG run was determined and used to determine the change in the activation energies DE, in each of the weight loss regions. A Plots of  $\ln(dw/dt)$  against  $1/T$  for the ligand and its metal complexes derivatives show straight lines. The activation energy, DE, can be estimated from the slope [15,19]. The energies of the thermal decomposition and melting of the ligand and its metal complexes are 10.6, 15.2, 14.8 and 15.6 Kcal/mol for  $\text{H}_2\text{BTS}$ ,  $[\text{Cu}(\text{BTS})]$ ,

[Co(BTS).2H<sub>2</sub>O] and [Ni(BTS).2H<sub>2</sub>O], respectively. The small difference in the energy of activation may be due to various factors, mainly differences in masses, particle size and experimental environments [23,24]. The activation energy for the ligand is less than metal complexes. The activation energy for copper complex is higher than those for cobalt and nickel complexes.

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