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Coordination Compounds of Co(II), Ni(II) and Cu(II) with Quadridentate Thiosemicarbazone: Their Preparation, Characterization and Structural Investigation

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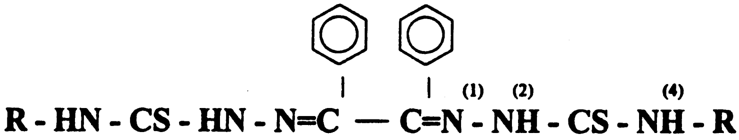
New transition metal complexes of Co(II), Ni(II) and Cu(II) with benzil-bis(4-ethyl thiosemicarbazone) and benzil-bis(4-butyl thiosemicarbazone) have been synthesized. Attempts have been made to ascertain their probable structures on the basis of elemental analysis, spectra (IR, electronic), thermal studies and magnetic measurements. The ligands can function as a binegative quadridentate (NSSN) with the metal ions forming complexes in molar ratio 1 : 1 having the empirical formulae ML and $ML\cdot 2H_2O$. The magnetic moment measurements and the crystal field parameters calculated for Co(II) and Ni(II) complexes agree fairly well with that reported for known octahedral complexes.

INTRODUCTION

Thiosemicarbazones are of current interest with respect to their biological activity and chemotherapeutic properties[1–4]. 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[5–11]. This paper investigates the chelating properties of benzil-bis(4-ethyl-thiosemicarbazone), H_2ETS, and Benzil-bis(4-butyl-thiosemicarbazone), H_2BTS, with cobalt(II), nickel(II) and copper(II) ions. The prepared thiosemicarbazones and their metal complexes may show biological activity. We have used elemental analyses, different spectroscopic techniques, magnetic measurements and thermal analyses to elucidate both stoichiometry and structure for the isolated compounds. In future work we aim to test our compounds for biological activity.

EXPERIMENTAL

The chelating agents, H_2ETS and H_2BTS, were prepared by mixing an ethanolic solution of benzil (0.1 mmole) and 4-ethyl-thiosemicarbazide (0.2 mmole) or 4-butylthiosemicarbazide in the same solvent. The reaction mixture was held under reflux in a water bath for 1.5 h, 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 EtOH and dried in a desiccator over silica gel. Yield 85%. Identification of H_2ETS and H_2BTS were done by elemental analysis and IR spectra (Structure I).



R = C_2H_5 or C_4H_9

(I)

The complexes were prepared by adding EtOH solutions of equimolar amounts of H_2ETS or H_2BTS and metal(II) salt. The mixtures were heated on a water bath for 2 h and allowed to evaporate slowly prior to filtration. The precipitates were washed with hot EtOH and dried Et_2O and preserved in a desiccator over silica gel. Yield 60–80%. Melting points for these solids are in the 182–213°C range.

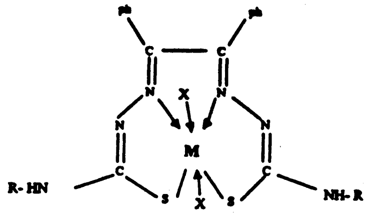
RESULTS AND DISCUSSION

The elemental analyses are inconsistent 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 IR spectra of the free ligands, H_2ETS and H_2BTS, exhibit absorption bands at 3196 cm^{-1} and 3245 cm^{-1} assigned to ν[N(2)H] and ν[N(4)H], respectively[5]. The thioamide group, (NH—C=S), gives rise to bands I–IV at 1534, 1325, 980 and 786 cm^{-1}. The strong band at 1534 cm^{-1} in the IR spectra of the free ligands is assigned to the combination of ν(C=N) and ν(C=C) modes[8]. The bands around 1325 and 786 cm^{-1} observed in the free ligands may be assigned to ν(C=S) vibration[8]. However, the cobalt(II), nickel(II) and copper(II) complexes lack any absorption due to ν(C=S) and ν[N(2)H], which implies deprotonation of the bis-thiosemicarbazones on coordination.

The disappearance of ν[N(2)H] and ν(C=S) with the simultaneous appearance of a new band in the region 1560–1550 cm^{-1} region and a weak new band at 615–610 cm^{-1} which is attributed to ν(C=N*) and ν(C=S),[5] repectively, indicates the involvement of the nitrogen and sulphur atoms in bonding to the metal ions through enethiolization.

The higher shifts in wave number of ν(N—N) by 5–15 cm^{-1} and the appearance of new bands in the low frequency region at 434, 440 and 448 cm^{-1} for the respective Ni(II), Co(II) and Cu(II) complexes due to (M←N),[2–4] confirms the participation of the azomethine nitrogen in bonding. All this may suggest structure II for the complexes.



M = Co(II) , Ni(II), X = H_2O
= Cu(II) , X = zero
R = C_2H_5 or C_4H_9

(II)

Electronic Spectra and Magnetic Measurements

The electronic spectra of the Ni(II) complexes show two bands at 24213 and 13495 cm^{-1} assigned to the $^3T_{1g}$ (P) $\leftarrow$ $^3A_{2g}(\nu_3)$ and $^3T_{1g}$ (F) $\leftarrow$ $^3A_{2g}(\nu_2)$ transitions, respectively.

The ν_1 position is found to be 9881 cm^{-1}; thus $\nu_2/\nu_1 = 1.37$. The D_q, B and μ_B values were calculated from the observed positions of the bands and are 988 cm^{-1}, 538.6 cm^{-1} and 0.52 respectively. These values together with the magnetic susceptibility (2.21 μ_B) support the octahedral structure[14].

The magnetic moment value (1.76 μ_B) for [Co(BTS)·$2H_2O$] is near the spin-only value for low-spin octahedral cobalt(II) complexes. The electronic spectrum has a strong peak around 23809 cm^{-1} which is due to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition[14]. The other charactersitic bands for d–d transition are difficult to recognize in this complex.

The electronic spectrum for [Cu(BTS)] complex shows a good three d–d transition. The spectrum shows a clear shoulder at 17543 cm^{-1} which may be due to a combination of $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in a square-planar configuration[14]. However, the strong band observed at 26315 cm^{-1} may be assigned as a charge transfer, probably, d–π*. Also, the broad band centered at 20618 cm^{-1} in the spectrum of [Cu(BTS)] may be due to Cu → L charge transfer[14].

The room temperature (23°C) magnetic moment (1.17 μ_B) for the copper(II) complex shows a subnormal magnetic moment which may arise from metal-metal interaction[15].

Thermal Analysis

The thermal behaviours of Ni(II), Co(II), Cu(II) complexes and H_2BTS were studied by TG and DTG. The TG thermograms of Co(II) complex (Fig. 1) show

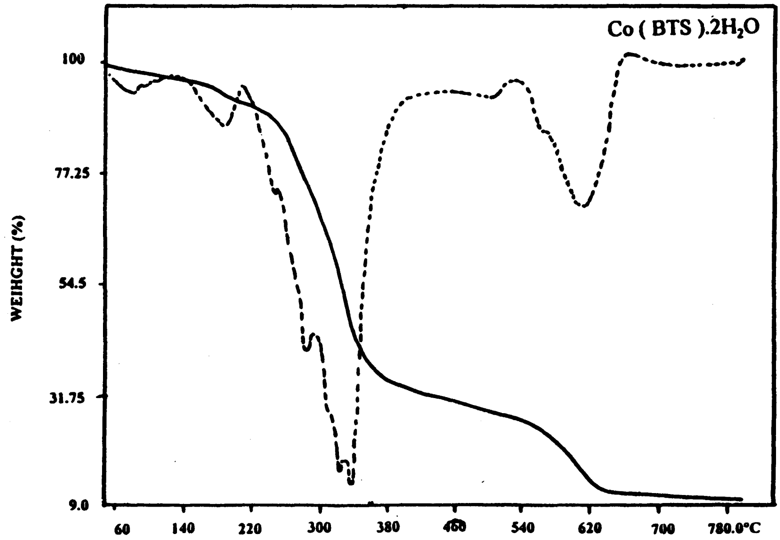


Fig. 1 DTG (.......) and TG (____) thermograms for Co(BTS) $2H_2O$ complex

a weight loss at 190°C (calcd. 6.42%, found 6.25%) corresponding to loss of water from the coordination sphere of the complex. The anhydrous thiosemicarbazone Co(II) complex begins to decompose from 190°C through different exothermic peaks at 245, 283, 323 and 337 up to 600°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°C.[16] The remaining mass is in good agreement with the calculated one.

Fig. 2. and Fig. 3 show the same behaviour of Ni(II) and Cu(II) complexes. The exothermic peak at 280°C is assigned to bond breaking between the metal ions and coordinated water molecules in [Ni(BTS)·2H_2O] complex (Fig. 2). The broad exothermic peaks at 360–400°C include various processes of decomposi-

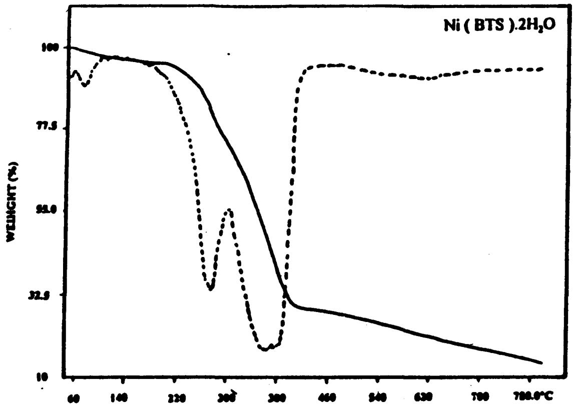


Fig. 2 DTG (.......) and TG (___) thermograms for Ni(BTS) 2H_2O complex

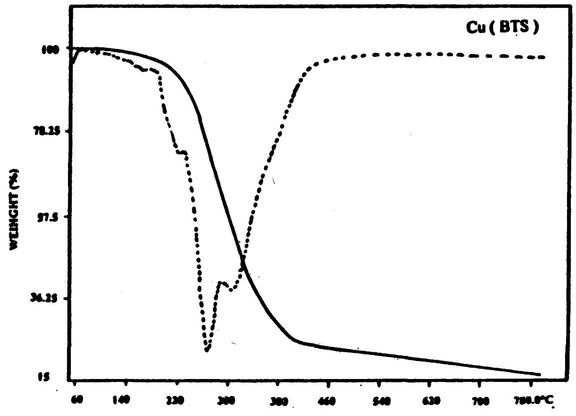


Fig. 3 DTG (.......) and TG (___) thermograms for Cu(BTS) complex

tion with the loss of the organic portion and the subsequent formation of the final NiO product.

Thermoanalytical methods are excellent tools to follow the thermal decomposition of the ligand and complex materials.

The weight per cent at each temperature in TG run was determined and used to determine the activation energies ΔE, in each of the weight loss regions. A plots of ln (dw/dt) against 1/T for the ligand and its metal complex derivatives show straight lines (Fig. 4). The activation energy from the slope can be estimated[17]. The energies of the thermal decomposition and melting of the ligand and its metal complexes are 4.36, 9.12, 8.87 and 8.66 kcal mol^{-1} for H_2BTS, Cu(BTS), [Co(BTS)·$2H_2O$] and [Ni(BTS)·$2H_2O$], respectively. The small difference in the energy of activation may be due to various factors, including mainly differences in masses and particle size and experimental enviroments[18, 19]. 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. The behaviour can be attributed to the difference in the atomic radii of the metals. The higher stabilities of the metal complexes than that of the ligand may be due to the formation of stable 5- and 6-membered ring structures in the metal complexes.

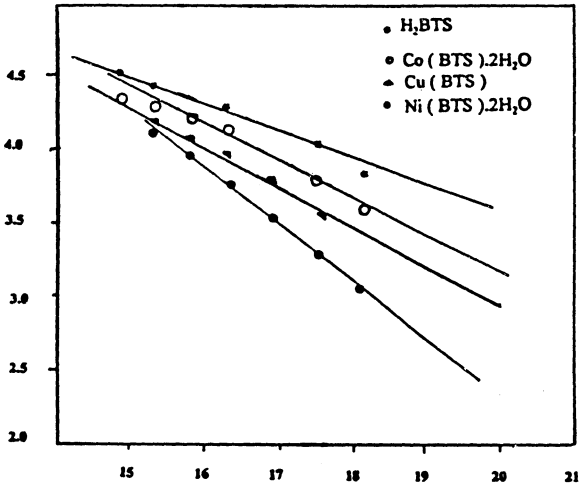


Fig. 4. A plot of ln (dw/dt) against (10^4/T) for H_2BTS and its metal complexes

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