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Research Article

Synthesis, Characterization and Kinetic Study of Monomeric Complexes of Cyclohexane-1, 2- bis (Thiosemicarbazone) with Cobalt (II), Nickel (II) and Copper (II)

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Abstract

Cyclohexane-1,2-bis(thiosemicarbazone) (CHTSC) was synthesized via the condensation reaction of cyclohexane-1,2-dione and thiosemicarbazide. Series of metal complexes of the prepared ligand, of general formula $[M(CHTSC)(NO_3)_2]$, were reported. The prepared coordination complexes were characterized and their structures elucidated using different techniques. These showed that all complexes are octahedral geometries. The kinetics of the formation of these complexes have been investigated using stopped-flow spectrophotometry. These studies revealed that the reactions are completed on the second's timescale with 1st-order dependence (either on the concentration of metal salt or on the concentration of CHTSC).

Keywords: Schiff base ligands, Thiosemicarbazones, Kinetic study.

الخلاصة

تضمن البحث تحضير ليكاند لقاعدة شيف من خلال التفاعل التكثيفي للسياكلوهكسان ثنائي اون والثايوسيمي كاربازايد. تم تحضير سلسلة من معقدات العناصر لليكاند المحضر ذات الصيغة العامة $[M(CHTSC)(NO_3)_2]$. تم تشخيص المعقدات التناسقية المحضرة وتم التوصل الى اشكالها الهندسية بأستخدام تقنيات مختلفة, حيث بينت الدراسة بأن جميع المعقدات المحضرة لها شكل هندسي ثماني السطوح. تمت دراسة حركية تكوين المعقدات والتي أظهرت التفاعل من المرتبة الأولى اعتمادا على كل من تركيز الليكاند او الأيون الفلزي.

Introduction

Compounds that are containing sulfur and nitrogen atoms (thiosemicarbazones) have received remarkable interests and extensive investigation due to their bonding modes and biological applications [1] [2] [3] [4] [5] [6] [7]. Thiosemicarbazone compounds are also applicable in several fields of inorganic chemistry. The commonly use as: a chelating agent for the formation of metal complexes. Moreover, the metal complexes of thiosemicarbazones have been applied in the field of material sciences such as nonlinear optical (NLO) [7] [8], electrochemical sensing [9], and Langmuir film [10]. During the recent twenty years, so may papers have been published reporting the synthesis and characterization of transition metal complexes with thiosemicarbazones [17]. In this paper, the synthesis, characterization and structural studies of cyclohexane-1,2-bis(3-thiosemicarbazone) (CHTSC) and its metal complexes with different transition metal ions like : Co(II), Ni(II) and Cu(II), are reported. Kinetic studies on the formation of the prepared complexes have been also investigated.

Materials and Methods

All reagents that have used in this work were commercially available (Aldrich Co.). Elemental analyses (C, H and N) were carried out on a EuroEA Elemental Analyzer. Electronic spectra were measured in the region (200–1,100) nm for solutions in DMF at room temperature using a Shimadzu, 100 UV–visible spectrophotometer. Infrared spectra were recorded using a Cary 630 FTIR spectrometer equipped with an ATR module.1H and ^{13}C NMR spectra were measured in DMSO–d_6 solution with the TMS as an internal standard, using a Brucker 400MHz. Metals were determined using a novaAA 350 flame atomic absorption spectrometer. Conductivity measurements were made with DMF solutions using a Inolab multi 740 digital conductivity meter. Magnetic moments of the prepared complexes were measured at RT using an auto magnetic susceptibility balance (Sherwood).

Preparation of CHTSC

A mixture of thiosemicarbazide (0.7 g, 8mmol) and cyclohexane-1,2-dione (0.4 g,4mmol) was dissolved in methanol (30 mL). The solution was heated under reflux for 4 h, during which a yellow precipitate was formed. This solid was filtered off and washed with hot methanol. Yield = 54 %, 0.5g, m. p = 212– 214 °C. Elemental analysis, found (calc.), C 37.95 (37.20), H 5.22 (5.42), N 32.20 (32.55) S 25.50 (24.80).1H NMR spectrum: δ/ppm:1.75-2.87 (cyclohexane protons, m, 8H); 7.75(H_2N–CSH, d, 2H); 8.6 (NH, s, 1H); 10.3 (H_2N–C =S, d, 2H); 12.22(SH, s, 1H).1^{3}C{^{1}H} NMR spectrum: 20.95-33.5 (cyclohexane carbons); 146.12 (C=N); 178.93 (C=S).

Synthesis of the complexes

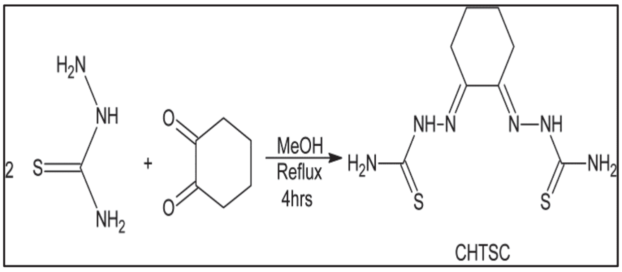
To a solution of CHTSC (0.15g, 0.58mmol) in acetonitrile (40 ml) was added the solution of metal salt (0.58mmol) [$Co(NO_3)_2.6H_2O$, 0.17g ; $Ni(NO_3)_2.6H_2O$, 0.17g ; $Cu(NO_3)_2.2.5H_2O$, 0.13g] in acetonitrile (5ml). A microcrystalline solid was formed immediately. This was filtered off and washed with acetonitrile. Microelemental analysis; yield and other properties for the complexes are listed in Table 1.

Kinetic studies

Applied Photo physics SX.18MV stopped-flow spectrophotometer was used to perform the kinetic studies. The solutions were prepared in MeCN at RT and used within 1 h of preparation. Pseudo-first-order conditions were applied for all experiments with the concentration of CHTSC in an excess over the concentration of the metal ion.

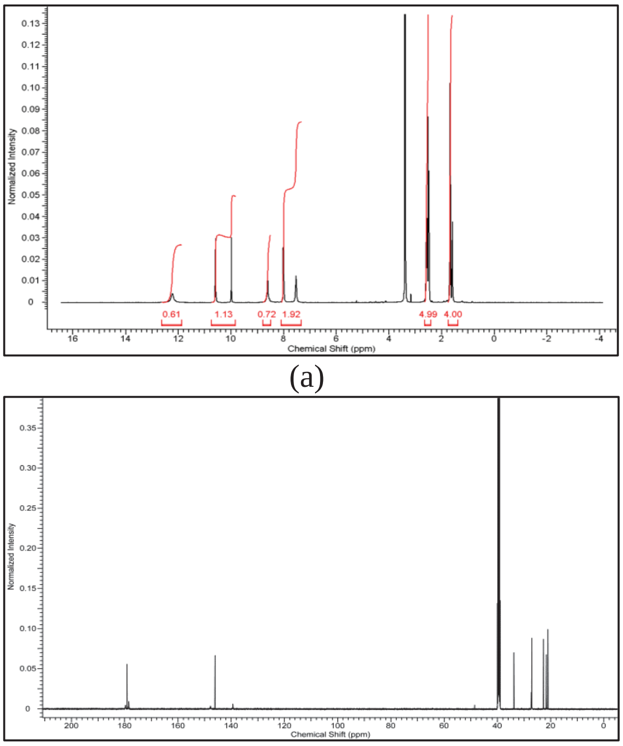
Results and Discussion

N_2S_2 type ligand, CHTSC (Scheme 1), was synthesized by the reaction of cyclohexane-1,2-dione and 3-thaiosemicarbazide.



Scheme 1: General route for the preparation of CHTSC.

Different spectroscopic techniques (elemental analysis and IR, ^{1}H and^{13}C NMR spectroscopies) were used to characterize the prepared ligand. Characteristic bands have been observed in the IR spectrum of the ligand which mainly belong to NH, NH_2 and C=N functional groups, Table 2. While, several signals are located at the ^{1}H and ^{13}C NMR spectra of the ligand. These signals are correspond to the various proton and carbon nuclei (see Experimental part and Figure 1). The UV–visible spectrum of CHTSC exhibited an intense absorption peak at (28571cm^{-1}) attributable to the (π-π*) transition.

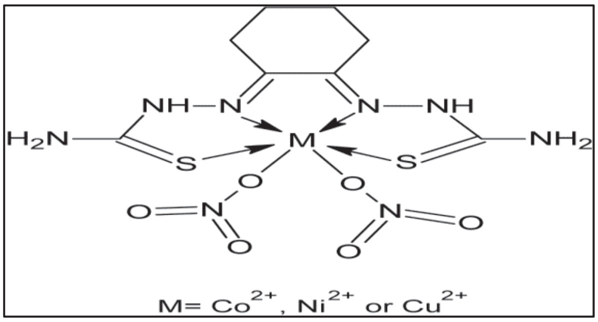


(a)

(b)

Figure 1: NMR spectra of CHTSC: a) ^{1}HNMR b)^{13}CNMR.

The reactions of equimolar amounts of CHTSC with a variety of divalent metal ions (M = Co,Ni or Cu), in a 1:1 stoichiometric ratio, produced rapid deposition of microcrystalline solids. However, the physical properties together with elemental analysis and molar conductivity values, Table 1, give an evidence that all the prepared complexes are neutral with the formulation [$M(CHTSC)(NO_3)_2$].



Scheme 2: Proposed molecular structures of the prepared complexes.

The IR spectrum of the free ligand (Figure2) shows bands in the region (3420–3110 cm^{-1}), which is attributed to the υ(NH) and υ(NH_2) vibrations. The bands due to υ(C=N) and υ(C=S) vibrations are located in the regions 1610 and 1360 cm^{-1}, respectively [18]. While, in the spectra of Schiff base complexes, the υ(C=N) mode of ligand is found to shift to higher wave numbers, suggesting the coordination of the azomethine nitrogen to the central metal ion, in agreement with previous studies [19] [20]. In the far infrared region, weak to medium bands have been observed around (610-510), (420–475) and (400–403) cm^{-1} in all the complexes. These could be assigned to the vibrations of υ (M-O), υ(M–N) and υ(M–S), respectively [21] [22] [23]. In addition, the spectra of complexes displayed two characteristic bans at the ranges: (1580 – 1450) cm^{-1}. These are due to the stretching vibrations of NO_3 group [24]. The most important infrared bands of the ligand and its complexes together with their assignments are collected in Table 2.

Table 1: Physical properties, elemental analyses and molar conductance values for the prepared compounds.

Compound	Color	Yield (%)	m. p.	Found (Calcd.) (%)					--
				M	S	C	H	N	Λ/(S cm^2 mol^{-1})
[CHTSC]	Yellow	54	212-214	–	25.50 (24.80)	37.95 (37.20)	5.22 (5.42)	33.20 (32.55)	–
[Co(CHTSC)(NO_3)$_2$]	Brown	58	290-293	14.30 (13.37)	15.23 (14.51)	22.30 (21.76)	3.55 (3.17)	26.32 (25.39)	9
[Ni(CHTSC)(NO_3)$_2$]	Brown	56	245-247	13.98 (13.28)	15.12 (14.52)	22.43 (21.79)	4.01 (3.17)	26.12 (25.42)	11
[Cu(CHTSC)(NO_3)$_2$]	Brown	63	233-235	13.92 (14.25)	15.20 (14.36)	22.21 (21.54)	3.88 (3.14)	26.20 (25.14)	13

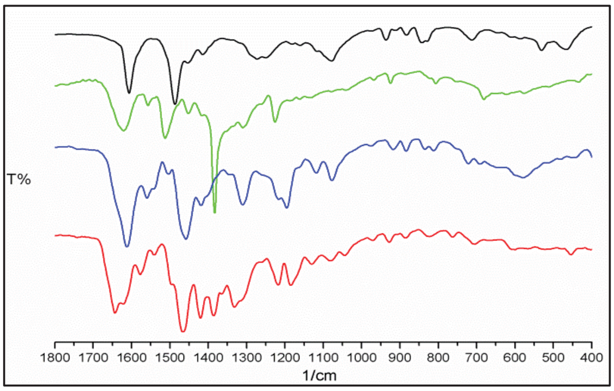


Figure 2: FTIR spectra: CHTSC (black), [Co (CHTSC) (NO_3)$_2$] (green), [Cu (CHTSC) (NO_3)$_2$](blue), [Ni (CHTSC) (NO_3)$_2$] (red).

In general, hypsochromic shifts of ligand bands were detected in all the electronic spectra of the prepared complexes (Figure 3). The electronic spectrum of the cobalt (II) complex in DMF solution exhibited absorption bands at (18867cm^{-1}), (15625cm^{-1}) and (14084cm^{-1}). These bands can be attributed to the $^{4}A_{2}g^{(F)}$ - $^{4}T_{1}g^{(P)}$, $^{4}A_{2}g^{(F)}$ - $^{4}T_{1}g^{(F)}$ and $^{4}A_{2}g^{(F)}$ - $^{4}T_{2}g^{(F)}$ transitions respectively [25] [26] [27]. Furthermore, the magnetic moment value of this complex is (3.80 BM). These data confirm the octahedral geometry around cobalt atom. Three absorption bands at (24390cm^{-1}), (15151 cm^{-1}) and (13333cm^{-1}) were observed in the he UV-Vis spectrum of the Nickel (II) complex. These may be assigned to the $^{3}T_{1}g^{(F)}$ - $^{3}T_{1}g^{(P)}$, $^{3}T_{1}g^{(F)}$ - $^{3}A_{2}g^{(F)}$ and $^{3}T_{1}g^{(F)}$ - $^{3}T_{2}g^{(F)}$ transitions respectively [25–27]. The position of these bands together with magnetic moment value (2.9 BM) revealed the octahedral geometry around nickel atom. While, two characteristic absorption bands at (20833cm^{-1}) and (18181 cm^{-1}) were located in the electronic spectrum of the Copper (II) complex. These bands can be assigned to the ^2B_1g- ^2Eg and ^2B_1g-^2B_2g transitions respectively. The magnetic moment value of this complex is (1.86 BM). These data confirm the octahedral geometry around copper atom [25] [26] [27]. The electronic spectral data, magnetic moment data and molar conductivity of (CHTSC) complexes are listed in Table 3.

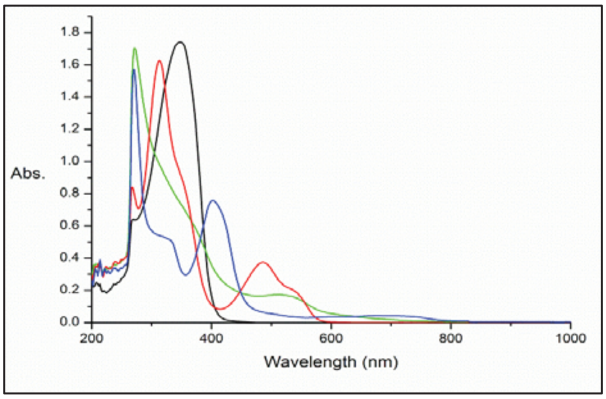


Figure 3: U. V- Vis spectra: CHTSC (black), $[Co(CHTSC)(NO_3)_2]$ (green), $[Ni(CHTSC)(NO_3)_2]$ (blue), $[Cu(CHTSC)(NO_3)_2]$ (red).

Table 2: IR frequencies (cm^{-1}) of the prepared compounds.

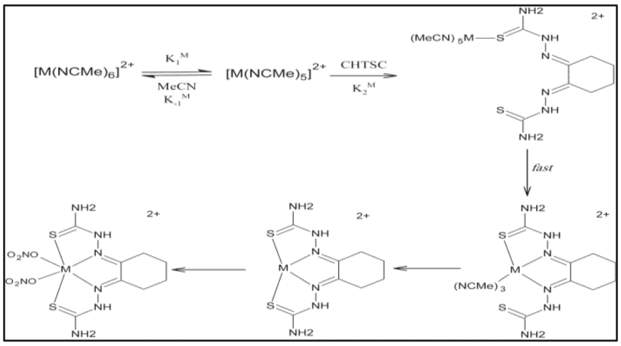
Compound	υN–H, (NH_2)	υ(C = N)	υ(NO3)	υ(M–O)	υ(M-N)	υ(M–S)
[CHTSC]	3420, (3225,3150)	1610	-	-		–
$[Co(CHTSC)(NO_3)_2]$	3415, (3255,3110)	1622	1550-1450	610	475	402
$[Ni(CHTSC)(NO_3)_2]$	3375, (3300,3150)	1640	1580-1540	510	420	403
$[Cu(CHTSC)(NO_3)_2]$	3390, (3250,3120)	1620	1560,1520	559	450	400

Table 3: Magnetic moments and UV-vis spectral data in DMF solution.

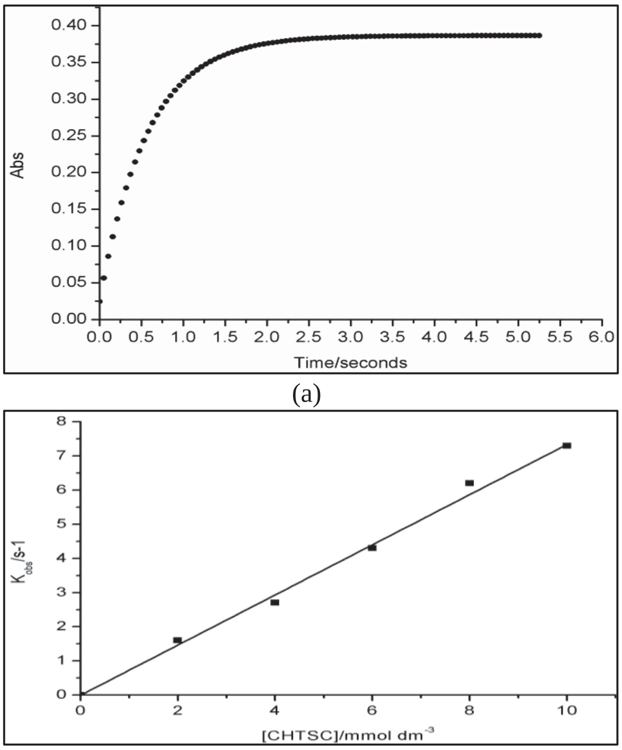
Compound	**($υ^-cm^{-1}$)**	**Extinction coefficient ($ε$, L mol^{-1} cm^{-1})**	**Assignment**	**$μ_{eff}$(BM)**
[CHTSC]	28571	1750	π-π*	-
$[Ni(CHTSC)(NO_3)_2]$	37735 24390 15151 13333	1570 700 70 20	π-π* $^3T_1g^{(F)}$-$^3T_1g^{(P)}$ $^3T_1g^{(F)}$- $^3A_2g^{(F)}$ $^3T_1g^{(F)}$- $^3T_2g^{(F)}$	2.90
$[Cu(CHTSC)(NO_3)_2]$	32258 28571 20833 18181	1620 900 390 200	π-π* CT ^2B_1g - ^2Eg ^2B_1g - ^2B_2g	1.86
$[Co(CHTSC)(NO_3)_2]$	34482 27777 18867 15625 14084	1700 1180 180 60 15	π-π* CT $^4A_2g^{(F)}$ - $^4T_1g^{(P)}$ $^4A_2g^{(F)}$ - $^4T_1g^{(F)}$ $^4A_2g^{(F)}$ - $^4T_2g^{(F)}$	3.80

Kinetic studies

Stopped-flow spectrophotometry was used to study the kinetics of the reactions between CHTSC and variety of metal ions: Co (II), Ni(II) or Cu(II). The reactions were studied under pseudo-first-order conditions with [CHTSC] ≥ 10[M^{2+}]. Figure 4, shows that the absorbance-time traces is fitted to a single exponential curve, which indicates a first-order of the reactions depending upon the concentration of metal ion. This conclusion is confirmed in studies where the concentration of metal ion was varied in the range 0.2–1.0 mmol dm^{-3} with [CHTSC] = 10 mmol dm^{-3}. For each different metal ion, all reactions displaying a first-order dependence on the concentration of CHTSC, as typified by the plot shown in (Figure 4) and the corresponding rate law in Eq. (1). A proposed mechanism for the reactions is shown in scheme 3.



Scheme 3: Proposed mechanism for the reaction of divalent metal ion and CHTSC in MeCN.



(a)

(b)

Figure 4: Kinetic data for the reactions of divalent metal ion with CHTSC in MeCN at RT.

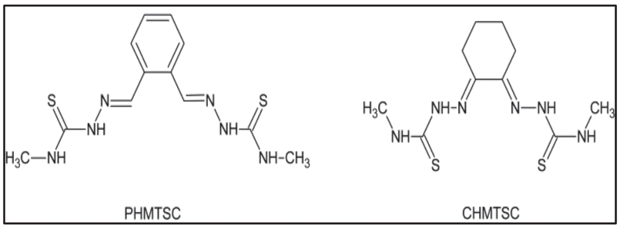
The example shown is for the reaction with Ni^{2+}. a) Shows an absorbance-time curve when $[Ni^{2+}] = 0.2$ mmol dm^{-3} and [CHTSC] = 2 mmol dm^{-3}. b) Shows the first order dependence of k_{obs} on the concentration of CHTSC. Straight line fit to the data is that defined by the equation $k_{obs} = 7.5 \times 10^{2}$ [CHTSC].

$$-d[M^{2+}]/dt = k_a^M [CHTSC][M^{2+}] \quad (1)$$

$$-d[M^{2+}]/dt = k_1^M k_2^M [CHTSC][M^{2+}] / k_{-1}^M [MeCN] + k_2^M [CHTSC] \quad (2)$$

$$-d[M^{2+}]/dt = k_1^M k_2^M [CHTSC][M^{2+}] / k_{-1}^M [MeCN] \quad (3)$$

Previous studies [16] [17] on other Schiff base thiosemicarbazones complexes [M(CHMTSC-$2H^{+}$)] and [M(PHMTSC-$2H^{+}$)] (where PHMTSC and CHMTSC have the structures shown below) have investigated the kinetic of the reactions of PHMTSC or CHMTSC with divalent metal ions. The rate constant k_a^M values for the reactions of CHTSC with metal ions, and the reactions of PHMTSC or CHMTSC with metal ions, are found to be quite close to each other. This may be due to the similarity in back bone structures of such type of ligands (slightly different).



As in PHMTSC and CHMTSC, and also other studies [28], the rate-limiting step of the chelate formation is the initial binding of CHTSC to $[M(NCMe)_5]^{2+}$ by replacing one of the coordinated CH_3CN molecules. The usual intimate mechanism for such a reaction is dissociative and involves initial dissociation of a coordinated solvent from $[M(NCMe)_n]^{2+}$, generating $[M(NCMe)_{(n-1)}]^{2+}$ containing a vacant site at which CHTSC can bind as shown in (scheme 3). The full rate law for this mechanism is shown in eqaution (2). When the concentration of CHTSC is small, k_{-1}^M [MeCN] $> k_2^M$ [CHTSC] the rate law would simplify to that shown in eqaution (3), which is of the same form as observed experimentally in eqaution (1). For each of the reactions studied, the values of $k_a^M = k_1^M k_2^M / k_{-1}^M$ [MeCN] are presented in Table 4.

Table 4: Rate constants for the reactions of CHTSC with divalent metal ion in MeCN at RT.

Metal ion M^2	**ka^M / dm^3 mol^{-1} s^{-1}**
Co	$4.5 \pm 0.5 \times 10^{2}$
Ni	$7.5 \pm 0.5 \times 10^{2}$
Cu	$8.3 \pm 0.5 \times 10^{2}$

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