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Synthesis, Characterization, and Thermal Behavior of 4-Chloromethyl-2-(2-Hydroxynaphthylidenehydrazino) Thiazole and its Complexes with Cr(III), Co(II), Ni(II), and Cu(II)

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A new ligand, 4-chloromethyl-2-(2-hydroxynaphthylidenehydrazino) thiazole, has been synthesized from dichloroacetone and 2-hydroxynaphthylidenethiosemicarbazone. Metal complexes of the ligand were prepared from acetate salts of Co(II), Cu(II), Ni(II), and chloride of Cr(III) in dry acetone. Characterization of the ligand and its complexes were made by microanalyses, FT-IR, ^{13}C, ^{1}H NMR, and UV-Visible spectroscopy, magnetic susceptibility, thermogravimetric analysis. In the light of these results it was suggested that two ligands coordinate to each metal atom by hydroxyl oxygen, imino nitrogen and thiazole ring nitrogen to form high spin octahedral complexes with Cr(III), Co(II), Ni(II), and Cu(II).

Keywords 4-chloromethylthiazole, 2-hydroxynaphthylidenehydrazine, 4-chlormethyl-2-(2-hydroxynaphthilidenehydrazino) thiazole, Cr(II), Co(II), Ni(II), Cu(II), complex

INTRODUCTION

It has long been known that metal ions involve in biological processes of life and has been the subject of interest. The modes of action of these metal ions are often complex but are believed to involve bonding to the hetero atoms of the heterocyclic residues of biological molecules, i.e., proteins, enzymes, nucleic acids, etc (Erwin and Omoshile, 1995).

Schiff bases and their metal complexes, played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical (Luo et al., 2003) and biochemically relevant studies of metal complexes (Murthy and Reddy, 1981; Streyer, 1995; Razakantoanina and Phung, 2000; Royer et al., 1995; Flack et al., 1993; Baumgrass et al., 2001; Quintana et al., 2000) and found wide range of applications. Thiazoles represent a very interesting class of compounds because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects, e.g., as antibacterial (Agarwal et al., 1997), fungicide (Sup et al., 1995; Buristrov and Bobashko, 1964), anti-inflammatory (Hadjipavlou-Litina and Geronikaki, 1996; Hadjipavlou et al., 1993; Geronikaki et al., 2003) antihelmintics, antitubercular (Merchant et al., 1981), anti-HIV (Maass et al., 1993), Antidegenerative (Anna et al., 2003) and hypothermic (Kapoor et al., 1984) activities and as herbicides (Metzger et al., 1984). In recent years thiazole based chemisensors have been investigated and showed to be successfuly applicable in biological systems (Santaun and Mini, 2000; Kim et al., 2000; Torrado et al., 1998; Thompson et al., 1996).

It is known that 2-aminothiazole is a biologically active compound with a broad range of activity and also is an intermediate in the synthesis of antibiotics and dyes. Numerous thiazole derivative Schiff bases and their transition metal complexes have been investigated by various techniques (Sitkowski et al., 1996; Castro et al., 1993; Saydam, 2002; Hidenori et al., 2001; Elisa et al., 2000; Saydam and Alkan, 2001; James et al., 1997; Mohamed, 2001).

From these points of view, it is important to study different types of transition metal complexes of these biologically active ligands. In this paper, the synthesis and characterizition of the first row transition metal complexes of the type [ML_2] $2H_2O$ where M is Cr(III), Co(II), Ni(II), and Cu(II) metals, L is a deprotonated ligand (4-chloromethyl-2-(2-hydroxynaphthylidenehydrazino) thiazole), have been studied.

EXPERIMENTAL

Thiosemicarbazide, 2-hydroxynaphthaldehyde, and dichloroacetone were purchased from Merck and used without further

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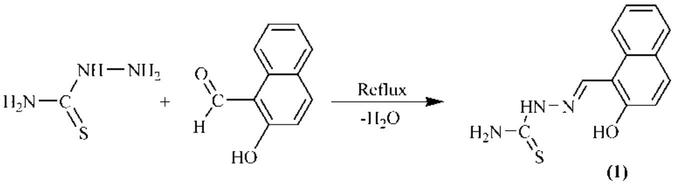
purification. The ligand synthesized was crystallized from ethanol and its purity checked by IR, NMR and elemental analysis. The elemental analyses were made by using a LECO-CHNS 932 microanalysis. IR spectrums were taken using Mattson 1000 FT-IR spectrophotometer as KBr pellets. ^{1}H and ^{13}C NMR spectrums were recorded on Bruker DpX-400 MHz spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance model MK1 at room temperature using $Hg[Co(SCN)_2]$ as a calibrant. Diamagnetic correction calculated from Pascal's constant. Thermogravimetric analyses were obtained from a Shimadzu TGA-50 Thermobalance. Melting points were determined on a Gallenkamp melting point apparatus. Electronic spectrums recorded on a Cecil CE 5502 Spectrophotometer in the quartz cell path length of 1.0 cm. Metal contents of the complexes were determined by an Ati Unicam atomic absorption spectrophotometer model 929, in a solution prepared by decomposing the complexes in concentrated hot $HCl + HNO_3$ mixture, then evaporating the solution and subsequent dilution with distilled water to desired volume.

Synthesis of the Ligand (LH)

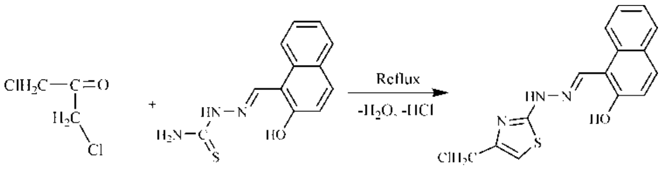
First, 0.064 mol (5.83 g) of thiosemicarbazide was dissolved in 150 ml of absolute ethanol in 250 ml flask. 0.064 mol (11.02 g) of 2-hydroxynaphthaldehyde dissolved in 50 ml dry ethanol was added drop-wise to this solution at room temperature, and then the solution was refluxed for 2 hours, then the temperature brought to room temperature and stirred for 24 hours. The mixture was poured to cold water and precipitate was filtered and washed with water and ethyl alcohol then dried at room temperature, yield 14.00 g (89%).



(1)

2-Hydroxynaphthylidene thiosemicarbazone (1)

Then, 0.04 mol (5.00 g) dichloroacetone was dissolved in 50 ml of dry acetone and added dropwise to 0.04 mol (9.65 g) of 4-chloro-2-(2-hydroxynaphthylidenehydrazino) thiosemicarbazone dissolved in 150 ml of absolute acetone at 0°C in an hour. Then it was stirred at room temperature for 24 hours followed by 2 hours' reflux. A green precipitate was filtered off and neutralized by 5% NH_3 solution, the color of the precipitate turns from light green to light yellow. After that the precipitate (Figure 2) was filtered, washed with ethanol, and water; dried at 60°C, yield 10.8 g (87%).



4-chloromethyl-2-(2-hydroxynaphthylidenehydrazino) thiazole (LH)

The characteristic IR bands (KBr pellets, cm^{-1}) are given in Table 1. The ligand found to be soluble in $CHCl_3$, THF, methanol, DMSO, DMF, acetone, ethyl acetate and insoluble in diethyl ether, n-hexane, and water, slightly soluble in ethanol. Characteristic ^{1}H NMR peaks are (CCl_4 TMS, δ ppm), 8.650 (s, –CH=N), 7.00 (s, =CH– in thiazole ring). Aromatic protons appeared at about 7.28–8.72 as multiplets. C–OH signal at 9.007 ppm, disappeared upon addition of D_2O to the solution, indicating that it is an acidic proton. The characteristic ^{13}C NMR peaks are: (CCl_4 TMS, δ ppm), 41.737 (C_1), 148.987 (C_2), 111.822 (C_3), 169.875 (C_4), 143.640 (C_5), 109.408 (C_6), 158.300 (C_7), 120.059 (C_8), 133.738 (C_9), 130.547 (C_{10}), 129.419 (C_{11}), 125.203 (C_{12}), 124.607 (C_{13}), 129.938 (C_{14}), 1132.870 (C_{15}). Anal. cal. for $C_{15}H_{12}ClN_3OS$ (317.80): C 56.69, H 3.81, N 13.22, S 10.09; found: C 56.46, H 3.74, N 13.54, S 10.66.

General Procedures for the Synthesis of the Complexes

First, 1 mmol of LH dissolved in 20 ml of absolute acetone then 0.5 mmol of acetate salt of metals dissolved in 10 ml of absolute ethanol (except $CrCl_3 \cdot 6H_2O$) was added drop-wise and refluxed for 4 hours, then neutralized by dilute NaOH solution. The precipitated complexes were filtered off washed with water and ethanol several times and dried at 60°C. The solid compounds were dissolved in 10 ml of tetrahydrofuran and reprecipitated in 100 ml of diethyl ether then washed with diethyl ether several times and dried in vacuum at 60°C. The complexes found to be soluble in $CHCl_3$, THF, DMSO, DMF, methanol, ethyl acetate, slightly soluble in 1,4-dioxane, dichloro methane, acetone, carbon tetrachloride, and insoluble in diethyl ether and petroleum ether.

The yield, color, melting point, and characteristic IR bands as KBr pellets, of the ligand and complexes are given in Table 1 and Table 2. Anal. cal. for $C_{30}H_{22}Cl_3CrN_6O_2S_2$, Mol. Wt.: 721.07, C, 49.93; H, 3.05; N, 11.65; S, 8.88, found: C 49.72, H 3.30, N 12.06, S 9.23, for $C_{30}H_{22}Cl_2CoN_6O_2S_2$, Mol. Wt.: 692.5, C, 52.03; H, 3.20; N, 12.14; S, 9.26, found: C 52.22, H 3.18, N 12.58, S 9.04, for $C_{30}H_{22}Cl_2NiN_6O_2S_2$, Mol. Wt.: 692.26, C, 52.05; H, 3.20; N, 12.14; S, 9.26; found: C 52.35, H 3.03, N 12.48, S 9.66; and for $C_{30}H_{22}Cl_2CuN_6O_2S_2$, Mol. Wt.: 697.12, C, 51.69; H, 3.18; N, 12.06; S, 9.20; found: C 52.02, H 3.16, N 12.32, S 9.51.

TABLE 1
Characteristic IR bands of the ligand and its complexes as KBr pellets

	Ligand (LH)	CrL_3	CoL_2	NiL_2	CuL_2
ν(O–H)	3454 br	—	—	—	—
ν(C=N) azomethine	1623 m	1616 s	1618 m	1616 m	1616 s
ν(C=N) (thiazole ring)	1567 s	1575 s	1579 s	1581 s	1579 s
ν(C–O)	1132 m	1097 m	1097 m	1097 m	1097 m
ν(C–S–C)	1034 w	1034 w	1041 w	1041 w	1034 w
ν(M–N)	—	621 w	631 w	631 w	633 w
ν(M–O)	—	569 w	525 w	532 w	569 w
ν(C–Cl)	743 w	746 w	746 w	746 w	746 w

Key: s (strong), m (medium), br (broad), w (weak).

RESULTS AND DISCUSSION

The synthesis of ligands (Figures 1 and 2) was performed in two steps. In the first step 4-chloro-2-(2-hydroxynaphthylidenehydrazino) thiosemicarbazone was obtained. In the second step the ligand molecule was formed by the ring closure reaction of 1,3-dichloroacetone and 4-chloro-2-(2-hydroxynaphthylidenehydrazino) thiosemicarbazone. Authentication of the ligand was checked by FT-IR, ^{1}H and ^{13}C NMR, elemental analysis. Then the coordination compounds were synthesized in dry acetone.

IR Spectra

Table 1 lists the major bands of the ligand and its complexes. In the IR spectra of the ligand (LH) the most characteristic bands appeared at 3454 cm^{-1} ν(O–H), 1567 cm^{-1} ν (C=N thiazole ring), 1623 cm^{-1} ν(C=N azomethine), and 1132 cm^{-1} ν(C–O), 1034 cm^{-1} ν(C–S–C) (Castro et al., 1993) and 748 cm^{-1} ν(C–Cl).

The azomethine vibration of the ligand at 1623 cm^{-1} was shifted to lower frequency after complexation, which is 1616, 1618, 1616, and 1616 cm^{-1} for Cr(III), Co(II), Ni(II), and Cu(II) complexes respectively. At the same time ν(C–O) band at 1132 cm^{-1} in the free ligand is shifted to lower frequency after complexation, which means that these shifts are due to coordination of ligand to metal atom over nitrogen of azomethine (Nakamura et al., 1979) and oxygen of hydroxyl groups. A broad band at 3400 cm^{-1} was observed in the spectra of the Cr(III) complex due to the presence of water molecule in the complex. The shifts of ν(C–O) band at 1132 cm^{-1} to lower energy suggests that the weakening of ν(C–O) and formation of stronger bond between M–O. The shifts of the ν(C=N) vibration of the thiazole group in all the complexes to lower energy suggest that nitrogen atom of the ring also contrubutes to the complexation. Practically unchanged ν(C–S–C) vibration at 1034 cm^{-1} of the thiazole ring (Castro et al., 1993) indicates that the thiazole group does not coordinate to metal from the sulfur atom. A weak band around 631 cm^{-1} in the complexes is absent in the ligand spectrum assigned to ν(M–O) vibration. Another weak band appeared in the spectra of the complexes at 525, 532, and 569 cm^{-1}attributed to ν(M–N) vibration (Williams and Fleming, 1989). From these observations it was suggested that, the azomethine nitrogen, the nitrogen atom in thiazole ring and hydroxy oxygen involve in the complexation reaction as donor atoms.

UV-Vis. Spectra and Magnetic Moments

The electronic spectrum of the Schiff base LH and its complexes were recorded in THF. Two very strong bands at 345 nm

TABLE 2
Formulas, formula weights, colors, melting points, yields, metal contents of the ligand and its complexes with transition metals of Cr(III), Co(II), Ni(II), and Cu(II)

Compounds	FW g/mole	Magnetic susceptibility BM	Color	Mp (°C)	Yield %
LH, $C_{15}H_{12}ClN_3O_2S$	317.80	—	Light green	201	87
CrL_2Cl, $C_{30}H_{22}Cl_3N_6O_4S_2Cr$	721.07	4.81	Dark brown	195	70
CoL_2, $C_{30}H_{22}Cl_2N_6O_4S_2Co$	692.26	2.87	Light brown	205	70
NiL_2, $C_{30}H_{22}Cl_2N_6O_4S_2Ni$	692.50	2.94	Light green	215	72
CuL_2, $C_{30}H_{22}Cl_2N_6O_4S_2Cu$	697.12	1.48	Dark green	150	58

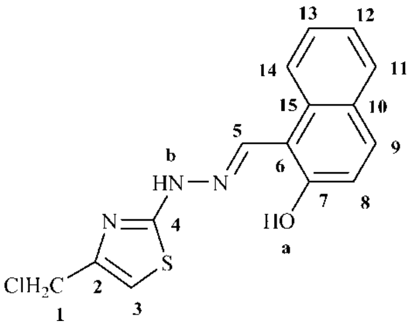


FIG. 1. 4-Chloromethyl-2-(2-hydroxynaphthylidenehydrazino) thiazole (LH).

and 240 nm were observed in the spectra of the ligand, which are attributed to n → π* and π → π* transitions in the aromatic ring and C=N chromophore (Drago, 1992). Chrome complexes have two absorption bands, 600, 400 and (as a shoulder) nm and assigned to $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$. The 10 Dq energy of the Cr(III) complex calculated from the Tanebe–Sugano diagrams was found to be 16670 cm^{-1} with a Racah parameter of 925 cm^{-1}. The observed magnetic moment value of 4.20 BM and the electronic spectra of the complex support the octahedral structure for the complex. The cobalt complex have two bands one at 740 nm and the other at 420 nm, which are assigned to $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. Calculated 10 Dq energy of the Co(II) complex is 1480 cm^{-1} and the Racah parameter is 600 cm^{-1}. From the position of the bands and the magnetic moment value of 4.8 BM the geometry of the cobalt complex is presumably octahedral. d-d transitions of the nickel complex at 625 nm and 420, corresponding to the transition of $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in the octahedral field were noted. Magnetic moment value of 2.9 BM supports the hexa coordinated configuration of the nickel complex. Calculated 10 Dq and the Racah parameters are 16390 and 595 cm^{-1}, respectively.

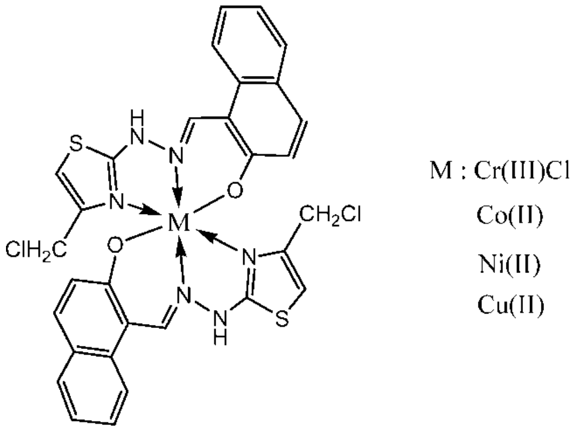


FIG. 2. Suggested structure of the Co(II), Ni(II), and Cu(II) complexes.

Cu(II) complexes display a wide range of geometries, often with a low symmetry and in most geometries the electronic spectra exhibits a very broad band with maximum which contains all the expected transitions (Greenwood and Earnshaw, 1984). The UV-visible spectra of the Cu(II) complex, has a strong band at 450 nm, assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition with a tailing to higher wavelength which is well known for octahedral copper complexes, (Elsonbatı et al., 1992; Mojumdar et al., 1999). The magnetic moment of 1.5 BM indicates some sort of molecular association that could be achieved through bridged ligand (Omar and Mohamed, 2005) or caused by spin orbit coupling.

The thermogram of the ligand shows that the weight loss begins at 230°C and decomposes at three steps, which are 230–260°C, 260–400°C and 400–750°C leaving 12% residue. The first step which has 6% weight lost corresponds to (–OH) group (calculted 5.4%). The second and third steps of the decomposition take place between 230–260°C corresponding to loss of 2-chloromethylthiazole group and the third step takes place between 400–750°C with the complete decomposition of the ligand.

All the complexes have similar decomposition pattern in two steps. In the first step 40% of weight loss between 225–380°C corresponds to the loss of 2-chloromethylthiazole (C_4H_3ClNS) group (calculated ≈38.5% for the all complexes). The complexes further decompose to yield 13.5%, 12.8%, 13.2%, and 12.3%, residue corresponding to Cr_2O_3 (calculated 10.9%), CoO (calculated 11.0%), NiO (calculated 10.9%), and CuO (calculated 11.3%), respectively.

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