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Polymeric complexes — LXI. Supramolecular structure, thermal properties, SS-DNA binding activity and antimicrobial activities of polymeric complexes of rhodanine hydrazone compounds

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ABSTRACT

A series of new ligands 5-(4′-alkylphenylazo)-3-phenylamino-2-thioxothiazolidin-4-one (**HL$_n$**) were synthesized from the coupling of 3-phenylamino-2-thioxothiazolidin-4-one with aniline and its *p*-derivatives. These ligands and their Co(II) polymeric complexes of the $[(Co)_2(\mathbf{L_n})_2(\mathbf{HL_n})(CH_3COO)_2(H_2O)_2]_n$ have been deduced from elemental analyses, IR, ^{1}H-NMR, X-ray diffraction and mass spectra as well as magnetic and thermal measurements. IR and ^{1}H NMR studies reveal that the ligands (**HL$_n$**) exist in the tautomeric enol/hydrazo form in both states with intramolecular hydrogen bonding. The important infrared (IR) spectral bands imply that **HL$_n$** is coordinated to the metal ion in a monobasic tetradentate *via* NH (hydrazone), oxygen of the carbonyl group (CO), nitrogen of the NH (3-phenylamine) and thion sulfur (CS) group. The complexes are polymeric, non-electrolytes, paramagnetic and octahedral six-coordinated. The molecular and electronic structures of the investigated compounds (**HL$_n$**) were also studied using quantum chemical calculations. The salmon sperm DNA (SS-DNA) binding activity of the ligands (**HL$_n$**) was studied by absorption spectra. The interaction between ligands (**HL$_n$**) and SS-DNA shows hypochromism effect coupled with obvious bathochromism. The values of binding constant are correlated with Hammett's constant (σ^R). The cytotoxic activity of ligands (**HL$_n$**) and their Co(II) complexes were tested against two human cancer HePG-2 (Hepatocellular carcinoma) and MCF-7 (breast cancer). The antioxidant activities of ligands (**HL$_n$**) and their Co(II) complexes were performed by ABTS method. The antimicrobial activity of ligands **HL$_n$** and their Co(II) complexes were tested against Gram negative bacteria (*Escherichia coli*), Gram positive bacteria (*Staphylococcus aureus*) and yeast (*Candida albicans*).

1. Introduction

In recent past, a variety of molecules based on rhodanine have been synthesized and evaluated with improved pharmacological activities due to their wide range of pharmacological and clinical utilization [1–8]. Rhodanine compounds and their complexes play an important role in biological reactions [9,10]. These molecules are considered as good antimycobacterial, antifungal, antidiabetic, antihepatitis C virus (HCV), anticancer, antioxidant, pesticidal, antihypertensive and antineoplastic agents. These molecules attracted much attention and encouraged the chemists and biologists to extensive investigations or molecular manipulations [5,11]. Chemical properties of rhodanine and its derivatives are of interest due to coordination capacity and their use as metal extracting agents; these molecules are capable of having keto–enol tautomers. Hydrazone compounds of rhodanine usually react as chelating with transition metal ions by bonding through the oxygen and hydrazinic nitrogen atoms [1,8], as they form a stable six-membered characterization of 5-(4′-alkylphenylazo)-3-phenylamino-2-thioxothiazolidin-4-one (**HL$_n$**) and their polymer complexes with cobalt(II). **HL$_n$** act as monobasic tetradentate reacting with Co(II) through the CO (rhodanine moiety), hydrazinic N with displacement of hydrogen atom, CS (rhodanine moiety) and amidic N.

DNA is one of the most important biomacromolecules in life processes because it carries inheritance information and instructs the biological synthesis of proteins and enzyme through the process of replication and transcription of genetic information. DNA plays an important role in the process of storing, copying and transmitting gene messages. DNA is also a major target for drugs and some harmful chemicals, and the studies on the binding nature of these small molecules to DNA are important and fundamental issues on life science because these drugs and chemicals can significantly influence the genetic information expression and result in some diseases

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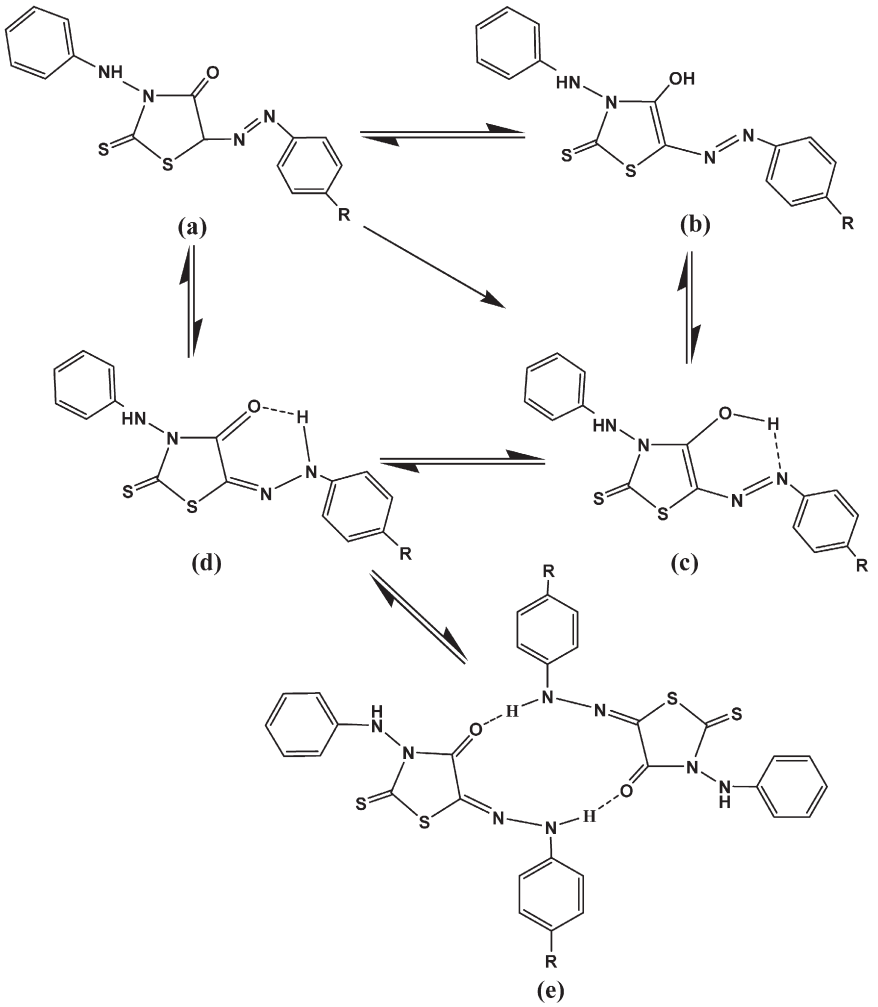

R = -OCH_3 (**HL_1**), -CH_3 (**HL_2**), -H (**HL_3**), -Cl (**HL_4**) and -NO_2 (**HL_5**)

Fig. 1. Structure of ligands (**HL_n**).

Table 1
Physical properties and elemental analyses data of the ligands (**HL_n**) and their Co(II) complexes (**1–5**).

Compound	M.P. (°C)	% Exp. (calc.)				Composition
		C	H	N	M	
HL_1	131	53.60 (53.63)	4.00 (3.91)	15.60 (15.64)	–	
(**1**)	–	46.22 (46.43)	3.56 (3.72)	12.12 (12.50)	8.37 (8.77)	$[(Co)_2(\mathbf{HL_1})(\mathbf{L_1})_2(CH_3COO)_2(H_2O)_2]_n$
HL_2	161	56.00 (56.14)	4.10 (4.09)	16.40 (16.37)	–	
(**2**)	–	48.03 (48.15)	3.66 (3.86)	12.74 (12.96)	8.78 (9.10)	$[(Co)_2(\mathbf{HL_2})(\mathbf{L_2})_2(CH_3COO)_2(H_2O)_2]_n$
HL_3	164	54.90 (54.88)	3.70 (3.66)	17.10 (17.07)	–	
(**3**)	–	46.77 (46.89)	3.35 (3.51)	12.04 (13.40)	(9.40)	$[(Co)_2(\mathbf{HL_3})(\mathbf{L_3})_2(CH_3COO)_2(H_2O)_2]_n$
HL_4	164	49.70 (49.66)	3.10 (3.03)	15.50 (15.45)	–	
(**4**)	–	43.14 (43.32)	2.89 (3.02)	12.03 (12.38)	8.47 (8.68)	$[(Co)_2(\mathbf{HL_4})(\mathbf{L_4})_2(CH_3COO)_2(H_2O)_2]_n$
HL_5	178	48.30 (48.26)	3.00 (2.95)	18.80 (18.77)	–	
(**5**)	–	42.12 (42.34)	2.87 (2.95)	14.86 (15.12)	8.15 (8.49)	$[(Co)_2(\mathbf{HL_5})(\mathbf{L_5})_2(CH_3COO)_2(H_2O)_2]_n$

[a]Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.
[b]The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.
[c]**HL_1–HL_5** are the ligands and **L_1–L_5** are the anions.