Nat. Volatiles & Essent. Oils, 2021; 8(6): 4738-4746

NVEO
Natural Volatiles &
Essential Oils

Synthesis, Characterization And Thermal Study Of New Schiff Base Ligand Derived From Thiazole And Its Complexes With [Ni II, Hg II And La III] Type N_2O

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Abstract:

In this work, 2-aminobenzothiazole reaction with benzoin in ethanol and drops of 48% HBr to procure the ligand [L] .2 mole of The ligand was refluxed in solvent with the metal ions [Ni^{+2} $Hg^{+2}$and La^{+3}] salts, using KOH as a base in (2:1) molar ratio to give the complexes. in EtOH to yield new complexes. The structure of synthesized complexes described via FTIR, UV-Visible Spectroscopy, TGA-DSC, Atomic Absorption, chloride content, conductivity and the elemental analysis (CHNS).the proposed geometrical structures for every prepared complexhave been of the octahedral formula.

Key-words: bezoin, 2-aminobenzothiazole, coordinated complexes

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Introduction

Benzoin (2-hydroxy-1,2-di(phenyl)ethanone) is an organic compoundwith the formula PhCH(OH)C(O)Ph,it is a hydroxy ketone attached to 2 phenyl groups(1,2),it appears as off-white crystals, with a light camphor-like odor. Benzoin is synthesized from benzaldehyde in the benzoin condensation. It is chiral and it occurs as a couple of enantiomers: (R)-benzoin and (S)-benzoin.Benzoin is not a constituent of benzoin resin obtained from the benzoin tree(Styrax) or tincture of benzoin. (3-5). The Thiazole is a versatile heterocycle, which is found in structures of several drugs in use in addition to the anti-cancer agents. The present paperpresents an overview of the recent developments in the thiazole-bearing complexes as anti-cancer agents with a specific focus on their mechanism of action in the cancerous cells(6-10). The chemical designs, relevant preclinical properties and structure–activity relationships were described in detail. Benzoin is utilized as well on the canker sores in and around the mouth for protecting them and enable them to heal(11-15). The Benzoin is utilized as well for helping to soothe and relieve the minor throat, nose, and airways irritations (such as croup and laryngitis) in the case of mixing it with the hot water and inhaling the steam. Benzoin is the sap (gum resin) that comes from cuts in the trunk of trees that to the styrax family

Benzoin is used on the skin for ulcers, cracked skin, bed sores (pressure ulcers), and several of the other conditions, however, there aren't any good scientific evidences for supporting those uses. Benzoin is used in small quantities in foods as a flavoring(16-18).

2.Experimental

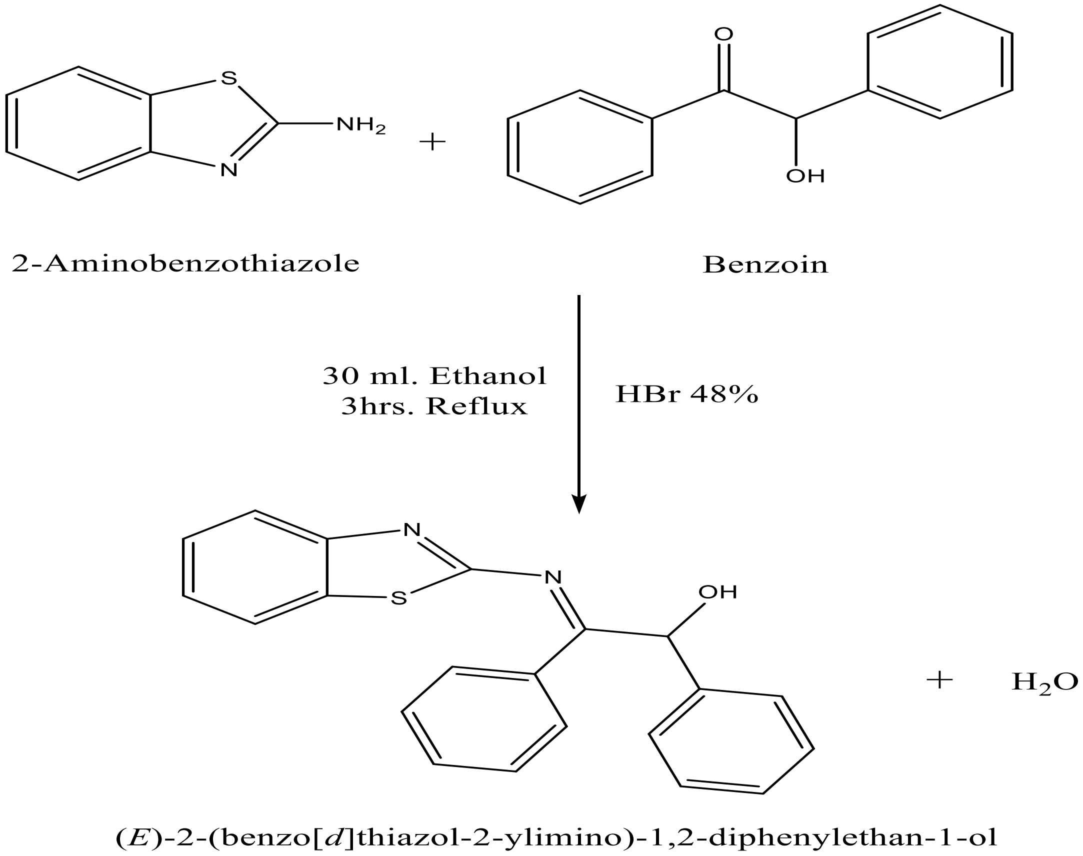
2.1.Materials: All of the chemicals have been brought from Fluka.

2.2.Arrangement: infrared Spectra recorded on a Shimadzu using potassium bromide disk . Thermal study TGA-DSC were studied and characterized. The C.H.N.S. were performed on an European Elemental .

2.3. Provision of components:

2.3.1.Creation of(E)-2-(benzo[d]thiazol-2-ylimino)-1,2-diphenylethan-1-ol

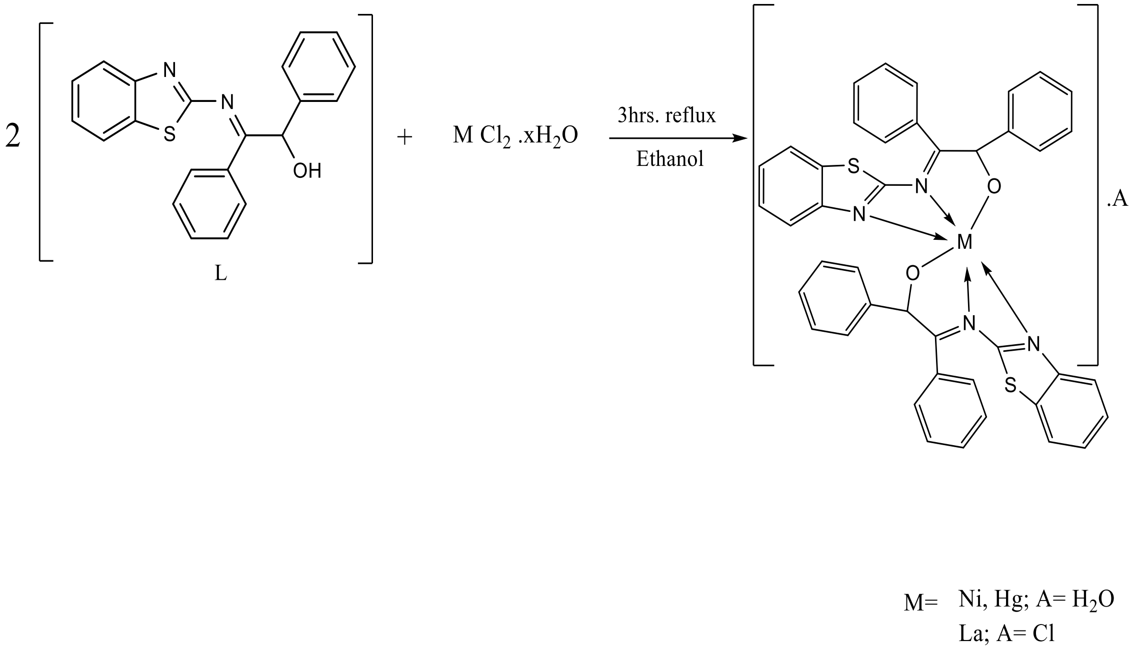
In a round bottom flask, 2-aminobenzothiazole (0.70g) in (15ml) ethanol and Benzoin (1g) dissolved in (15ml) ethanol and adding drops of 48%HBr , then reflux for 3 hours under nitrogen blanket,(by water bath 80 ^{0}C and strring) then filtration and recrystallized to produce yellow precipitate ,produce (85%) , Melting point=172-174 ^{0}C , scheme (1).



Scheme (1) synthesis of ligand (L)

2.3.2.Synthesis of Metal Developments [Ni(II),Hg(II) and La (III)] with lig and (L)

The (1:2) component metal and (L) have been synthesized via melting (0.145 g.) (L) in (15ml) of the total solvent, then assorted with solution containing (0.2 g.) metal chloride salts dissolved in the utter solvent (15 mL). The fusion refluxed a dated (3hrs.) on water bath under nitrogen blanket, on the cooling of the contents, the complexes have been divided out. The invention has been filtered, then it was wash away by the solvent and dehydratedby using the rotary, Scheme (2).



scheme (2) synthesis of complexes.

3. Results and Discussion

3.1. FTIR of compounds

In pattern (1), Compound [L] was produced through the countering of 2-aminobenzothiazole reaction with Benzoin and sodium nitrate in solvent. FT-IR of compound [L] show the presenceclutches at (1677) cm^{-1} mention to (C=N) and vanishingof 2 absorption groupsat (3444 and 3194cm^{-1}) owed to symmetric and asymmetric extending of (-NH$_2$) group correspondingly fig.(1). In scheme Synthesis some TMC [Ni(II), Hg(II) and La(III) of this component. All complexes have been synthesized by reaction of 2 mole compound[L] and metal salt in ethanol.FT-IR of complexes [Ni(L)$_2$] (H$_2$O), [Hg(L)$_2$] (H$_2$O), [La(L)$_2$]C, fig.(2,3 and 4) displayed the shifting of band at (1679) cm^{-1}due to (C=N) group to higher and shifting of bands at (1068cm^{-1}) that are connected to stretching (C-O) group, at last appearance of bands at (418cm-^{1}-420cm-^{1}) due to (M-O) and at (502-497) cm^{-1} due to (M-N) confirming the coordination of metal with donor atoms. Table (1) show FT- IR spectrum of compounds$^{(18-21)}$.

Table (1): The characteristic infrared bands forcomponents

	Color	M.P.	υ(C=N) imine	υ(C-O)	υ(C=N) in plane	υ(M-O)	υ (M-N)
L	**yellow**	**102-107**	**1677**	**1066**	**1630**	**--**	**---**

L+Ni	**Light green**	**124-126**	**1679**	**1068**	**1650**	**418**	**501**
L+Hg	**brown**	**156-160**	**1679**	**1068**	**1614**	**422**	**507**
L+La	**Off white**	**92-95**	**1679**	**1068**	**1650**	**420**	**497**

3.2.Electronic Spectral data for the complexes :

The UV-Visible of ligand[L] fig. (5) spectra consideredmostly by 2 mountains of absorption at (222nm, 252nm) gave to (π → π *) & (n → π*)respectively. These electronic transition have been movedto lower orhigher frequencies in UV of every primed complex, prove the ligand's organization with the ions .

ElectronicNi (II) composite fig.(6) spectrum has shown peaks of absorption, those peaks at (240nm and 262nm) can be given to the intra – ligand. The peak at (692nm) has been a result of (d-d) type of the electronic transition $^{3}A_{2}g \rightarrow {}^{3}T_{1}g$whereas the final top at (762nm)$^{3}A_{2}g \rightarrow {}^{3}T_{2}g$. These peaks have been in respectablearrangement of the Oh geometry for the Ni(II)complex.

The Hg(II) complex'selectronic spectrum fig.(7) shows the peaks ofabsorption at (230, 260) nm raises to (π → π *) ,(n → π*) respectively , the metal ion of those types of the complexes be owned by d^{10} system and this metal showed no (d-d) electronic transition .

The electronic spectrum of La(III) complex fig.(8) showed the peaks ofabsorption at (224 nm, 256nm)raises to (π → π *) ,(n → π*) and charge transfer correspondingly , the metal ion of these types of the complexes belong to d^{0} system and this metal showed no (f-f) electronic transition[22-25] .

Table (2) the electronic results of compounds and conductivity

Compounds	conductivity	λ(nm)	υ- (cm^{-1})	εmax L/mol.cm	Transitions
L	-----	222	45045	1395	π→π*
		252	39682	836	n→π*
$[Ni(L)_2](H_2O)$	neutral	240	41666	4000	π → π*
		262	38167	4000	n→π*
		692	14450	19	$^{3}A_{2g} \rightarrow {}^{3}T_{1g}$

		760	13157	22	$^3A_{2g}\rightarrow{}^3T_{2g}$
$[Hg(L)_2](H_2O)$	neutral	230	43478	4000	$\pi \rightarrow \pi^*$
		260	38461	2582	$n\rightarrow\pi^*$
$[La(L)_2](Cl)$	1:1	224	44642	2443	$\pi \rightarrow \pi^*$
		256	39062	3175	$n\rightarrow\pi^*$

3.3. Thermal Decomposition of the ligand (L) and $[Ni(L)_2]$ H_2O

3.3.1 Thermal Decomposition of the ligand (L)

The thermogram for $C_{21}H_{16}N_2OS$has been illustrated in Fig. (9). In TGA curve, peak which has been recognized at 168.47 ºC is associated with the loss of (C_2H)amounts, (obs. = 0.80mg, 7.363%; calc. = 0.81mg). The second step at (242.1)°C is associated with the loss of (C_2H) portions, (obs. = 0.80mg, 7.333%; calc. = 0.81mg). The third step at (389.35)°C is associated with the loss of ($C_7H_6N_2S$) portions, (obs. = 4.79mg, 43.607%; calc. = 4.81mg) .the fourth step at (594.409)°C is associated with the loss of (CH_4O)portions, (obs. = 1.03mg, 9.466%; calc. = 1.04mg). The final remainder of the compound which has been observed higher than 594.409 ºC is assigned to (C_9H_4), (obs. = 3.58 mg, 32.55%; calc. = 3.59mg). The DSC curve of the analysis has proven that the peaks at 83.3, 280, 320°Cindicate aprocess of the endothermic decomposition. The peaks that have been observed at 262.20, 299.5, 500 ºC were related to exothermic decomposition processes(26).

3.3.1 TD of $[Ni\ (C_{21}H_{17}N_2O2S)_2]$

The thermo gram for $[Ni\ (C_{21}H_{15}N_2OS)_2]$ H_2O is illustrated in Fig. (10). In TGA curve, peak documented at 330.148 ºC is associated with the defeat of (H_2O, $4(C_6H_5)$, CO, C_2H) portions , (obs. = 7.98 mg, 49.886%; calc. = 7.99 mg) The second step at 594.886°C that designated the loss of ($C_8H_8N_2O$) amount, (obs. = 4.08mg, 25.541%; calc. = 4.09mg) The final remainder of the compound which has been observed higher than 594.886 °C is assigned to ($NiC_7HN_2O_2S$), (obs. = 4.27 mg, 26.72%; calc. = 4.28mg). The curve of theDSC analysis has proven that the peaks at 104.5, 254.5, 284.9 °Cindicate aprocess of the endothermic decomposition. The peaks that have been observed at 215, 260, 420 °Chave beenassociated with theprocesses of the exothermic decomposition. The endothermic and exothermic peaks canshow the ignition of the natural ligand in the argon atmosphere. The last endothermic pinnacle can imply the breaking of the metal-ligand bond (27-30)

Table (3) thermal analyses of ligand (L) and $[Ni(L)_2]$ H_2O

Complex	Stages	Temperature of Decomposition Initial-Final (^oC)	Estimated (calculated)		Assignments
			Mass Loss	Total mass Loss	
L	1	60-168.47	0.80 (0.81)	3.58 (3.59)	(C_2H)-
	2	168.47-242.1	0.80 (0.81)		(C_2H)-
	3	242.1-389.359	4.79 (4.81)		$C_7H_6N_2S))$-
	4	389.35-594.40	1.03 (1.04)		-(CH_4O)
$[Ni (L)_2]H_2O$	1	90-330.148	7.98 (7.99)	4.27 (4.28)	-(H_2O) $(C_{27}H_{21}O)$
	2	330.148-594.88	4.08 (4.09)		- (CH_3O_2)

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