

Nickel Complexes of Thiosemicarbazone Derivatives of Lawsone

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ABSTRACT

Thiosemicarbazone derivative at 1 position of the Lawsone (2-hydroxy-1,4-naphthalenedione) i.e. 1-TSCND is an important derivative, Which possesses a powerful chelating ability, appreciable analytical utility and significant biological activity^[1]. Its Nickel (II) complex is newly reported here.

INTRODUCTION

Most of the d block metals possess variable oxidation state. They formed coloured compounds with ligand possessing O O or O N donor systems. Therefore, they show charge transfer spectra in the visible region^[2,3]. Nickel - sulfur interaction have gain considerable interest of their green nickel in number of salts. While the sulphur containing ligands show more activity. The parent ligand i. e. Lawsone is coloured and its derivatives are also show different colors with different shades. The tridentate O N S ligating system of thiosemicarbazones can provide a thione or thiolato sulphur center while the napthalenedione segment may compliment for constructing this center gives stability to the metals like Nickel^[4].

Thiosemicarbazones are unique amongst the sulphur family of ligating systems⁵ not only because they possesses a wide range of biological properties^[5], but also due to the fact that their complexes exhibits various structural, electronic as well as biological potentials^[6]. The coupled chromophore of quinone - thiosemicarbazones probably may increases the covalent character in metal - ligand bonding^[4]. Metal complexes of sulphur containing Schiff bases has been the subject of current and growing interest because of it has been shown that many of these complexes possess anticancer activity. In a particular, thiosemicarbazones, as a class of compound exhibit a several interesting physical, chemical and wide range of biological properties. We report here 1-TSCND complex with Ni(II) metal.

EXPERIMENTAL**1-TSCND (2-hydroxy-1,4-naphthalenedione-1-thiosemicarbazone)**

1-TSCND is synthesized according to the procedure described earlier^[4,6,7]. As given in Figure 1.

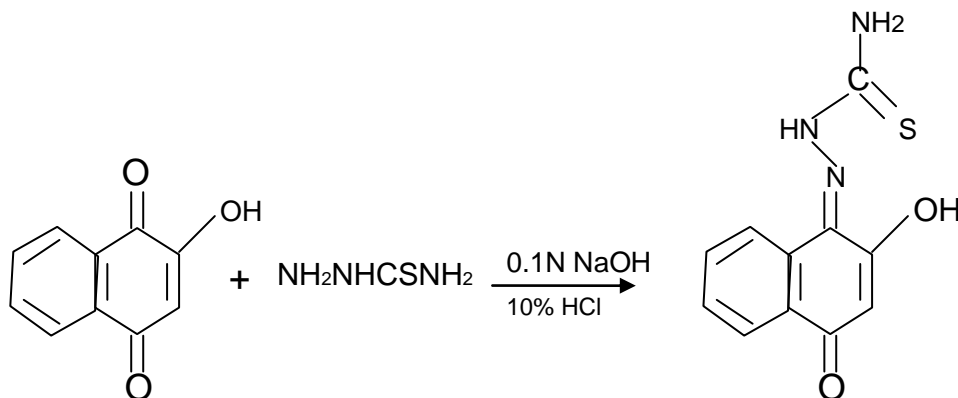


Figure 1: Lawsone 1-TSCND

To a water solution of Lawsone (0.01mol), 10 ml of 0.1 N NaOH was added so as to obtain a dark red solution. An aqueous-methanolic(50%) solution of thiosemicarbazone (0.01 mol) was then added dropwise to the above solution with constant stirring. The mixture was further stirred for about 3 hours, at the end of which, the solution was neutralized with 10 % HCl, until precipitation. The crude product thus obtained was recrystallized from aqueous methanol and dried under vacuum over CaCl₂ yielding reddish yellow crystalline product.

Yield: 7.8 gm(85%), m. p. - 214°C., Analysis: Calculated for C₁₁H₉N₃O₂S; C, 53.48; H, 3.67; N, 16.99; S, 12.97. Found C, 52.90; H, 3.70; N, 16.30; S, 13.30. IR (KBr) in cm⁻¹: 3375; υ (O-H), 2565; υ (S-H), 1668; υ (C=O), 1641; υ (C=N), 1280; υ (C=S), 1217; υ (C-O), 869; υ (C-S). ¹HNMR (CDCl₃) in δ ppm: 8.2 (T, 2H, -NH₂), 7.8 (m, 1H, C-3-H), 7.4 (s, 1H, C-5-H and C-8-H), 7.25 (s, 1H, C-6-H and C-7-H), 6.4 (s, 1H, C-2-OH) and 1.85 (s, 1H, -SH).

MATERIALS AND METHODS

All chemicals used were of A. R. or equivalent Grade. Solvents used were purified by literature methods^[8]. Ligand is purified by column chromatography using silica gel. Lawsone were purchased from Fluka A. G.

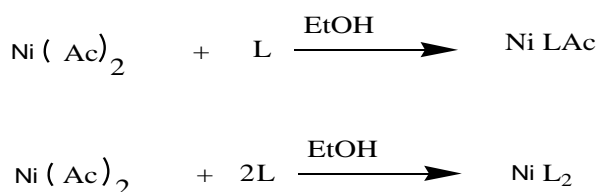
The elemental analysis for the percentage of carbon, hydrogen and other elements were performed in the micro analytical section using Flash EA, C, H, N and S Analyzer instrument, in the Agharkar Research institute, Pune.

The electronic spectra were recorded in ethyl alcohol on using Shimadzu UV-300 spectrophotometer model using 1 cm matched quartz cell. The Infra Red spectra were recorded in KBr on FTIR Shimadzu - 8400. The ¹H NMR spectra of ligand were recorded on VARIAN MERCURY YH - 300 MHz IN CDCl₃ in the Department of Chemistry, Pune. The structures of Ni complexes is simulated by using Cambridgesoftware (Chemoffice 2008 - Chem3D ultra 8.0 followed by MM2) for to measure bond length.

RESULTS AND DISCUSSION

General and Analytical

An aqueous solution 0.01 mole (1.768 gm) of Nickel acetate react with the ethanolic solution of 0.01 mole of ligand (2.47 gm of) and 0.02 mole of ligand (4.94 gm) refluxed in oil bath for three hours to yield the product Ni complexes as NiLAc and NiL₂ respectively (Scheme 1).



Scheme 1

The complexes show the dark brown and dark gray colour with 75 and 80 % yield respectively. These complexes are sparingly soluble in non-polar solvents like n-hexane, carbon tetrachloride etc., moderately soluble in polar solvents like methanol

and water but appreciable soluble in strongly coordinating solvent like DMF or DMSO. Both complexes containing adsorbed water. The elemental analysis data is presented in Table 1.

Table 1: Analytical Data of the complexes

Complex/ Mol. Wt.	Yield% Decomp. Temp.°C	Analysis Found (Calculated)				
		C %	H %	N %	S %	M %
Ni(L)Ac						
C ₁₃ H ₁₁ O ₄ N ₃ S ₁ Ni	75	41.70	3.45	10.39	8.06	15.89
363.71	210	(42.89)	(3.02)	(11.54)	(8.79)	(16.14)
Ni(L) ₂						
C ₂₂ H ₁₈ O ₄ N ₆ S ₂ Ni	80	48.50	3.90	14.11	10.22	10.01
552.71	230	(47.76)	(3.25)	(15.19)	(11.57)	(10.62)

Infrared Studies

Infrared spectroscopy is one of the important techniques utilized in quinone chemistry for the identification of various form of quinones in metal chelates^[9,10]. The Infrared spectra of ligand and the complexes were recorded in the region 4000 cm⁻¹ to 300 cm⁻¹. These frequencies include ν (O-H), ν (N-H), ν (C-O), ν (C=O), ν (S-H), ν (C=C), ν (Ni-O), ν (Ni-S) and ν (Ni-N).

(O-H) stretching frequency

In the spectra of L ligand, the frequency observed at 3375 cm⁻¹, due to presence of ν (O-H) stretching absorption^[11,12]. It is not observed in the spectra of complex Ni(L)Ac and Ni(L)₂. It indicates that coordination through (ν C-O) with central metal Nickel. The broad band is observed in the region 3400 – 3000 cm⁻¹, it may be due to adsorbed water. The short band at 3325 cm⁻¹ is observed in the spectra of ligand and its complexes, which is characteristics of secondary amine ν (ν N-H) absorption. However, (ν N-H) vibration from the same linkage disappear. It may be due to deprotonation resulting in the forming thiolato Sulphur centre.

(C=O) stretching frequency

The quinone carbonyl stretching is observed at 1668 cm⁻¹ in ligand. This band is shifted to lower frequency by ~ 30 cm⁻¹ in the spectra of Nickel complex.

(C-O) stretching frequency

In the spectra of ligand, ν (C-O) stretching frequency is observed at 1217 cm⁻¹, which is shifted to higher region by ~ 36 cm⁻¹ in the complex. It is due to back bonding effect. The strengthening of band after complexation, conforms the participation of phenolato oxygen in the coordination.

(C=N) and (S-H) stretching frequency

The band observed at 1641 cm⁻¹ in the spectra of ligand is assign to ν (C=N) stretching frequency^[13]. This band is shifted at 1589 cm⁻¹ for the complex. The band at the region 2565 – 2540 cm⁻¹ observed in the ligand is due to thiolato(ν S-H) stretching frequency. This band is not observed in the both complex. It is conformed that thiolato sulphur is involved in the coordination.

(C=S) and (C-S) stretching frequency

The small shoulder band is observed at 1280 – 1244 cm⁻¹ is attributed to thione ν (C=S) stretching frequency^[14] in the ligand. It is not observed in the spectra of complexes. The another frequency at 869 – 796 cm⁻¹ is attributed to ν (C-S) stretching frequency in the ligand. It shows red shift after complexation by 10 – 50 cm⁻¹. It conforms the sulphur is involved in the coordination.

(Ni-O), (Ni-N) and (Ni-S) stretching frequency

The three new bands are observed in the range 520 – 500 cm⁻¹, 486 – 440 cm⁻¹ and 400 – 374 cm⁻¹, which are attributed for the ν (Ni-O), ν (Ni-N) and ν (Ni-S) frequencies^[14] respectively.

Other frequencies

The band found in the region 1500 – 1400 cm⁻¹ in the spectra of ligand and their Nickel (II) complexes are assigning for aromatic ring vibrations. The absorption in the region 1290 – 1275 cm⁻¹ is observed because of quinone moiety characteristics^[15,16].

The electronic spectra of the ligand and their Nickel (II) complexes in ethanol are presented in Table 2. The electronic spectra of the ligand shows intense band at 238 – 240 nm and 358 – 392 nm, which are due to $\pi - \pi^*$ transition.

Table 2: Electronic Spectral data

Name of Complex	$\pi - \pi^*$		$n - \pi^*$
	BET	QET	LMCT
Ni(L)Ac	221.6	272.2	440.0
Ni(L) ₂	238.4	267.2	437.6

In which first and third bands are may be due to benzenoid electron transfer (BET) and second band is due to quinonoid electron transfer (QET)^[17]. After complexation with Nickel (II), this band shows slightly lower wavelength. The new band of low intensity is observed in the region 437 – 440 nm, which due to $n - \pi^*$ transition. It is referred as ligand to metal charge transfer (LMCT)^[3].

The d-d transition could not be assigned probably due to the charge transfer bands.

Proposed Structure for Ni[L]Ac

Probable structure of Ni[L]Ac complex in the square planar geometry as given in Figure 2. The bond length (Å) in Ni(L)Acis given in Table 3.

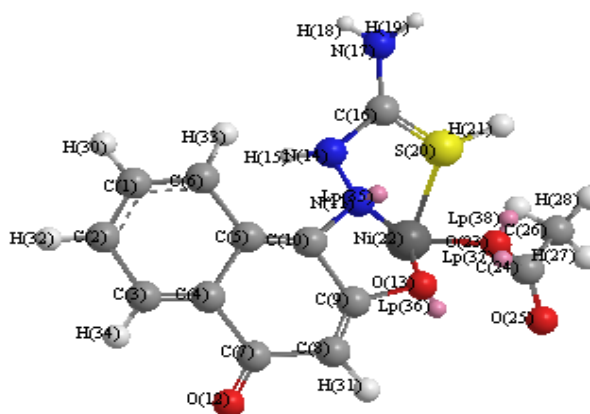


Figure 2: Probable Squire Planar Structure of Ni(L)Ac

Table 3: Bond lengths(Å) in Ni(L)Ac

C(1)–C(2)	1.417	C(8)–C(9)	1.323	N(17)–H(18)	1.028
C(1)–C(6)	1.416	C(8)–H(31)	1.121	N(17)–H(19)	1.028
C(1)–H(30)	1.124	C(9)–C(10)	1.656	S(20)–Ni(22)	2.232
C(2)–C(3)	1.663	C(9)–O(13)	1.551	S(20)–H(21)	1.424
C(2)–H(32)	1.124	C(10)–N(11)	1.451	Ni(22)–O(23)	1.832
C(3)–C(4)	1.325	N(11)–N(14)	1.359	O(23)–C(24)	1.422
C(3)–H(34)	1.123	N(11)–Ni(22)	1.877	O(23)–Lp(37)	0.647
C(4)–C(5)	1.682	N(11)–Lp(35)	0.688	O(23)–Lp(38)	0.643
C(4)–C(7)	1.704	O(13)–Ni(22)	1.819	C(24)–O(25)	1.216
C(5)–C(6)	1.661	O(13)–Lp(36)	0.651	C(24)–C(26)	1.549
C(5)–C(10)	1.327	N(14)–C(16)	1.508	C(26)–H(27)	1.122
C(6)–H(33)	1.121	N(14)–H(15)	1.028	C(26)–H(28)	1.122
C(7)–C(8)	1.700	C(16)–N(17)	1.525	C(26)–H(29)	1.122
C(7)–O(12)	1.213	C(16)–S(20)	1.542		

Proposed Structure for Ni[L]₂

Probable structure of Ni[L]₂ complex in Capped Trigonal Prism geometry as given in Figure 3 and bond angles are displayed in Table 4.

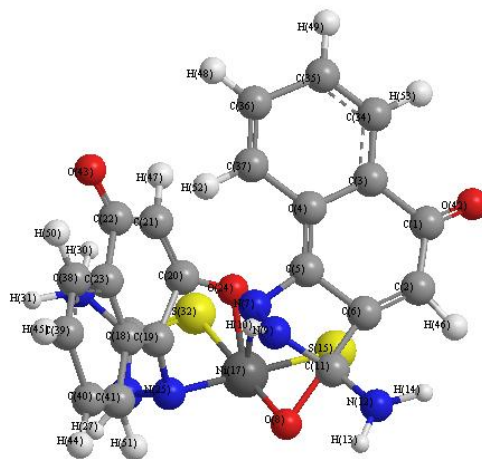


Figure 3: Probable Capped Trigonal Prism Structure of Ni(L)₂

Table 4: Bond lengths(Å) in Ni(L)₂

C(1)-C(2)	1.454	C(21)-H(47)	1.122	C(5),O(24)	1.639
C(1)-C(3)	1.540	C(22)-C(23)	1.540	C(5),S(32)	3.175
C(1)-O(42)	1.213	C(22)-O(43)	1.213	C(6),N(9)	2.807
C(2)-C(6)	1.324	C(23)-C(38)	1.540	C(6),C(11)	2.296
C(2)-H(46)	1.122	N(25)-N(26)	1.352	C(6),S(15)	1.552
C(3)-C(4)	1.540	N(26)-C(28)	1.446	N(7),C(19)	2.231
C(3)-C(34)	1.386	N(26)-H(27)	1.028	N(7),C(20)	1.637
C(4)-C(5)	1.324	C(28)-N(29)	1.446	N(7),C(21)	2.724
C(4)-C(37)	1.540	C(28)-S(32)	1.510	O(8),N(9)	2.229
C(5)-C(6)	1.540	N(29)-H(30)	1.028	O(8),C(11)	1.750
C(5)-N(7)	1.446	N(29)-H(31)	1.028	O(8),N(12)	2.594
C(6)-O(8)	2.989	C(34)-C(35)	1.386	N(9),C(19)	2.544
N(7)-N(9)	1.352	C(34)-H(53)	1.122	N(9),C(20)	2.576
N(7)-Ni(17)	1.826	C(35)-C(36)	1.652	N(9),O(24)	2.472
O(8)-Ni(17)	1.790	C(35)-H(49)	1.122	S(15),H(46)	2.663
N(9)-C(11)	1.446	C(36)-C(37)	1.324	C(18),C(39)	2.896
N(9)-H(10)	1.028	C(36)-H(48)	1.122	C(19),C(22)	2.852
C(11)-N(12)	1.446	C(37)-H(52)	1.122	C(19),C(28)	2.691
C(11)-S(15)	3.066	C(38)-C(39)	1.324	C(20),C(23)	2.874
N(12)-H(13)	1.028	C(38)-H(50)	1.122	C(20),C(28)	2.579
N(12)-H(14)	1.028	C(39)-C(40)	1.602	C(20),S(32)	2.587
S(15)-Ni(17)	2.170	C(39)-H(45)	1.122	C(20),C(37)	2.805
Ni(17)-O(24)	1.790	C(40)-C(41)	1.324	C(20),H(52)	1.976
Ni(17)-N(25)	1.826	C(40)-H(44)	1.122	C(21),C(37)	2.459
Ni(17)-S(32)	2.170	C(41)-H(51)	1.122	C(21),H(52)	1.347
C(18)-C(19)	1.386	C(2),C(4)	2.865	C(23),C(40)	2.896
C(18)-C(23)	1.386	C(2),S(15)	2.288	O(24),C(28)	2.606
C(18)-C(41)	1.540	C(3),C(6)	2.864	O(24),C(37)	2.673
C(19)-C(20)	1.540	C(4),O(24)	2.342	O(24),H(52)	2.386
C(19)-N(25)	1.446	C(4),C(35)	2.852	C(36),H(47)	2.539
C(20)-C(21)	1.324	C(5),C(11)	2.655	C(37),H(47)	1.929
C(20)-O(24)	1.410	C(5),S(15)	2.339	H(47),H(52)	0.992
C(21)-C(22)	1.530	C(5),C(20)	2.654		

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