



SYNTHESIS, SPECTRAL, THERMAL AND ANTIFUNGAL STUDIES OF NICKEL (II) COMPLEXES OF O,N DONOR LIGANDS

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ABSTRACT :

The solid complexes of Ni^{II} with Schiff bases derived from 3-acetyl-6-methyl-(2H)-pyran-2,4(3H)dione (dehydroacetic acid) and aromatic amines, have been synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic, IR, NMR, UV-VIS spectral studies and X-ray powder diffraction. From the analytical data, the stoichiometry of the complexes has been found to be 1:2 (metal: ligand). The low conductance values suggest that the complexes are non-electrolytes. IR spectral data suggest that the ligand behaves as a bidentate ligand with N:O donor sequence towards metal ions. The kinetic parameters (*n*, *E*, *Z*, ΔS and *G*) estimated using Coats-Redfern (C.R), Mac Callum-Tanner (M.T.) and Horowitz Metzger (H.M.) methods are in good mutual agreement. The powder X-ray diffraction study suggests that the complex has monoclinic crystal system. The physico-chemical data suggests that all the complexes possess square planer geometry. The ligands and their Ni^{II} complexes are also screened for antifungal activity.

KEYWORDS : Dehydroacetic acid, Transition metal complex, Ni^{II} complexes, Schiff bases, Thermal analysis, Powder X-ray diffraction.

INTRODUCTION

Schiff bases have a central role as chelating ligands in main group and transition metal coordination chemistry [1]. They deserve proper attention because of their role in biological applications and excellent chelating ability [2,3]. The extensive work in solid coordination complexes has been made possible with the help of various experimental techniques and has led to a number of interesting conclusions [4]. Dehydroacetic acid is an important biologically active compound, since it has antibiotic, fungicidal [5], antiseptic [6] effects and used to enhance vitamin 'C' stability and protect vegetables during food processing [7]. It is well known from the literature that dehydroacetic acid moiety have a strong ability to form metal complexes and its Schiff bases show very interesting biological properties [8-11]. Coordination of such compounds with nickel metal ion often enhance their activity [12,13].

To the continuation of our research on dehydroacetic acid [14-16] we report herein the synthesis, thermal, spectral and antifungal activity of new Ni^{II} complexes of Schiff bases (1-8) (Fig. 1) derived from dehydroacetic acid and aromatic amines.

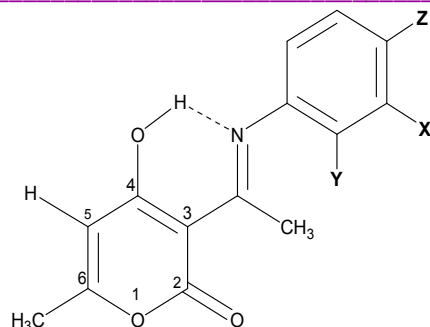


Fig. 1 : The Proposed structure of the ligands

Experimental

All the chemicals and solvents used in all preparative and analytical works were of A.R. grade. Dehydroacetic acid used for the preparation of ligand is of Merck. The micro analytical data for carbon, hydrogen, nitrogen content in each sample were recorded on Elemental Analyzer Perkin Elmer (2400), I.r spectra (nujol) in the range of $4000\text{--}450\text{ cm}^{-1}$ were recorded on Perkin Elmer (C-75430), ^1H NMR spectra of the ligand were measured in CDCl_3 . The AAS, TGA-DTA and XRD were recorded on Perkin Elmer PE-Analyst 300, TG/DTA-2960 and Philips 1701 respectively. The UV-VIS spectra of the complexes were recorded on Shimadzu UV-1601 spectrophotometer. Magnetic susceptibility measurements of the complexes were carried out using a Gouy's balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Molar conductivity was measured on a conductivity meter EQ-660 with a dip-type cell using 10^{-4} M solution of complexes in DMF.

Synthesis of ligand

The ligands here synthesized by mixing equimolar solution of dehydroacetic acid and aromatic amine in ethanol and the mixture was reflux for 6 hours. The content was cooled to room temperature. The solid so obtained was separated washed and recrystallized from ethanol (yield 52-61%). The purity of the ligand were checked by TLC, melting point, elemental analysis and confirmed by i.r and PMR.

Synthesis of metal complexes

To a hot solution of the ligand (2mmol) in (30ml) methanol, the metal chloride (1mmol) in (20ml) methanol was added drop wise with stirring. It was then refluxed for 2- 4 hours. The pH of the reaction mixture was maintained to 7.5 – 8.0 by adding 10% methanolic solution of ammonia.. The resulting metal complex was filtered in hot condition and washed with methanol, pet-ether ($40^\circ\text{C}\text{--}60^\circ\text{C}$) and dried over calcium chloride in vacuum desiccator (yield 63-70%).

RESULTS AND DISCUSSION:

All the complexes are pink colored solids, stable to air and are non-hygroscopic. They decompose at high temperature without melting. They are insoluble in water and moderately soluble in common non-polar organic solvents. They have low molar conductance values ($<10\text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) in 10^{-4} M solution of metal complexes in DMF, shows that the metal complexes are non electrolytes in nature [17]. The elemental analysis reveals mononuclear nature and 1:2 composition of M:L. The analytical results of complexes are presented in Table1.

Table 1: Analytical data, molecular weight and melting point of ligand and their Ni^{II} complexes.

Molecular formula of Ligand/Complexes	% Yield	Found (Calculated)					F.W.	M.P °C	λ_m Mho cm ² mol ⁻¹
		C	H	N	Cl/Br	M			
C ₁₄ H ₁₂ ClNO ₃ (L1)	57	59.80 (60.55)	3.68 (4.36)	4.65 (5.04)	11.86 (12.77)	-	277.71	120	-
C ₁₄ H ₁₃ NO ₄ (L2)	52	64.01 (64.86)	4.49 (5.05)	4.51 (5.4)	-	-	259.26	188	-
C ₁₅ H ₁₅ NO ₄ (L3)	58	64.96 (65.93)	5.12 (5.53)	4.94 (5.13)	-	-	273.29	108	-
C ₁₅ H ₁₅ NO ₃ (L4)	56	69.20 (70.02)	5.47 (5.88)	5.02 (5.44)	-	-	257.29	118	-
C ₁₄ H ₁₂ BrNO ₃ (L5)	54	51.85 (52.20)	3.47 (3.75)	4.02 (4.35)	23.87 (24.80)	-	322.16	138	-
C ₁₅ H ₁₃ NO ₅ (L6)	53	61.98 (62.72)	4.45 (4.56)	4.51 (4.88)	-	-	287.27	238	-
C ₁₆ H ₁₇ NO ₄ (L7)	61	66.18 (66.89)	5.80 (5.96)	4.36 (4.87)	-	-	287.32	118	-
C ₁₄ H ₁₁ Cl ₂ NO ₃ (L8)	58	53.21 (53.87)	3.11 (3.55)	4.30 (4.49)	21.64 (22.72)	-	312.5	164	-
[C ₂₈ H ₂₂ Cl ₂ N ₂ O ₆ Ni]	70	54.10 (54.94)	3.24 (3.62)	4.05 (4.58)	11.05 (11.58)	9.04 (9.59)	614.1	>270	01.8
[C ₂₈ H ₂₄ N ₂ O ₈ Ni]	64	57.85 (58.47)	3.65 (4.21)	4.01 (4.87)	-	9.65 (10.20)	575.19	>270	01.5
[C ₃₀ H ₂₈ N ₂ O ₈ Ni]	63	58.77 (59.73)	4.12 (4.68)	3.94 (4.64)	-	9.26 (9.73)	602.25	>270	00.5
[C ₃₀ H ₂₈ N ₂ O ₆ Ni]	65	62.81 (63.08)	4.42 (4.94)	4.02 (4.90)	-	9.73 (10.27)	571.25	249	00.8
[C ₂₈ H ₂₂ Br ₂ N ₂ O ₆ Ni]	67	47.12 (47.98)	2.91 (3.16)	3.79 (4.00)	22.25 (22.80)	8.12 (8.37)	700.99	>270	00.8
[C ₃₀ H ₂₄ N ₂ O ₁₀ Ni]	64	56.95 (57.08)	3.45 (3.83)	4.00 (4.44)	-	9.07 (9.30)	631.21	>270	01.6
[C ₃₂ H ₃₂ N ₂ O ₈ Ni]	69	60.32 (60.88)	4.49 (5.11)	4.01 (4.44)	-	9.14 (9.30)	631.3	>270	00.9
[C ₂₈ H ₂₀ Cl ₆ N ₂ O ₆ Ni]	63	48.95 (49.39)	2.49 (2.96)	3.98 (4.11)	19.87 (20.82)	8.44 (8.62)	680.17	>270	00.7

¹H-n.m.r. spectrum

The ¹H-NMR spectra of the ligands have been recorded in CDCl₃. The spectra of ligands shows sharp peaks for common protons in all ligands at $\delta = 2.17$ to 2.45 (s, 3H, pyran C6-CH₃), $\delta = 5.77$ - 5.81 (s, 1H, pyran C5-H), $\delta = 15.47$ - 15.94 (s, 1H, Enolic OH for DHA moiety) and $\delta = 2.40$ to 2.61 (s, 3H, CH₃-C=N). The phenyl moiety values observed $\delta = 6.95$ to 7.95 (m, 4H, for Ar-H). Beside these, L2 shows $\delta = 4.38$ (s, 1H, of phenolic OH), L3 shows $\delta = 3.81$ (s, 3H of CH₃), L4 shows $\delta = 2.60$ (s, 3H of CH₃), L6 shows $\delta = 10.51$ (s, 1H of COOH) and L7 shows $\delta = 3.18$ (q, 2H of CH₂) and $\delta = 1.39$ (t, for 3H of CH₃).

I.r spectra

The i.r. spectrum of the ligand shows bands at 3362 - 3364 cm⁻¹, 1702 - 1715 cm⁻¹, 1650 - 1660 cm⁻¹, 1436 - 1440 cm⁻¹ and 1220 - 1247 cm⁻¹ (Table 2) are assigned to ν OH (hydrogen bonded), ν C=O (lactone), ν C=N (azomethine) ν C-N (aryl azomethine) and ν C-O (enolic) vibrations respectively[18,19]. In the IR spectra of metal chelates no band is observed in the region 3362 - 3364 cm⁻¹ indicates the deprotonation of enolic -OH and subsequent bonding of its oxygen with Ni during complex formation. Coordinated site is supported by downward shift in ν C=N azomethine [20] and upward shift of ν C-O (enolic) [21] frequency. The new bands appeared in the region 611 - 620 and 512 - 520 which were absent in ligand may be due to formation of M-N and M-O bonds [22]. The above arguments indicate that the ligands behave as bidentate and coordinate to metal ions through enolic oxygen and azomethine nitrogen.

Table 2: Salient features of IR spectral data of Ni^{II} complexes, IR spectral data of corresponding ligands are shown in bracket.

Bond vibrational mode Stretching (ν)	band position of Ni(II) complexes (corresponding ligands) in wave number cm^{-1}								
	L1	L2	L3	L4	L5	L6	L7	L8	
O-H---N (bonded)	(3364)	(3362)	(3371)	(3368)	(3370)	(3364)	(3364)	(3367)	
C=O (lactone carbonyl)	1703 (1702)	1723 (1715)	1712 (1714)	1709 (1697)	1739 (1714)	1708 (1702)	1712 (1702)	1743 (1695)	
C=N(Azomethine group)	1633 (1650)	1654 (1660)	1654 (1663)	1631 (1649)	1645 (1663)	1631 (1646)	1651 (1661)	1634 (1663)	
C=C Aromatic ring	1582 (1575)	1582 (1580)	1582 (1578)	1582 (1574)	1581 (1578)	1581 (1575)	1582 (1571)	1582 (1575)	
C-N(Aryl azomethine)	1445 (1440)	1475 (1436)	1475 (1460)	1452 (1428)	1453 (1436)	1452 (1439)	1475 (1455)	1445 (1448)	
C-O (Enolic)	1246 (1227)	1244 (1220)	1325 (1247)	1243 (1220)	1245 (1228)	1246 (1228)	1244 (1226)	1256 (1220)	
New bands	M-O	615 (-)	617 (-)	668 (-)	606 (-)	600 (-)	596 (-)	620 (-)	620 (-)
	M-N	518 (-)	515 (-)	514 (-)	512 (-)	512 (-)	520 (-)	511 (-)	522 (-)

Magnetic and electronic absorption spectra

All the Ni^{II} complexes in present investigation are diamagnetic in nature. In the complexes the electronic absorption bands appeared in the region 17006-17543 cm^{-1} and 25773-27778 cm^{-1} are assigned to $^1A_{1g} \rightarrow ^1T_{2g}$ transition and charge transfer transition respectively. These facts support the square planer geometry [23]. The absence of band below 10,000 cm^{-1} is in favor of square planer geometry [24].

Thermal study

The complex of ligand L3 and L5 are chosen for thermal study. Thermogravimetric analysis does not show a weight loss up to temperature 300°C, which indicates the absence of coordinated water and water of hydration. The TG curve of L3 complex shows that the first exothermic peak occurs at 327°C and second at 556°C. The complex shows high thermal stability and absence of lattice or coordinated water as its decomposition starts at 300°C. It follows double step decomposition. In the first step the complexes undergo steady weight loss of 68.0% (calc.68.43%) from 300-400°C temperature which may be due to the reaction interval corresponding to the decomposition of organic ligand part. In the second step the complex undergo weight loss of 16.0% (calc.16.52%) from 400-600°C temperature which may be due to the decomposition of chelated part. Beyond 600°C a stable end product with mass 14.5% (calc.15.05%) equivalent to NiO₂ is remains indicated by horizontal line.

The TG curve of L5 complex reveals that there is no weight loss up to 300°C. It appears to decompose in two steps the first exothermic peak occurs at 330°C and second at 582°C. The first step decomposition begins at ~300°C and continues up to 400°C shown by sudden weight loss of 72.5% (calc.72.75%). It is due to decomposition of large part of organic ligand and its subsequent oxidation. In the second step the complex undergo weight loss of 12.0% (calc.12.20%) from 400-600°C temperature which may be due to the decomposition of chelated part. Beyond 600°C a stable end product 15.5% (calc.15.05%) equivalent to NiO₂ is remains indicated by horizontal line.

In order to calculate the kinetic parameters viz. n (order of reaction), E (Energy of activation), Z (pre exponential factor), $\ln S$ (Energy of activation) and G (Free energy change), three methods have been used namely, Coats Redfern (C.R) [25], Mac Callum-Tanner (M.T.) [26] and Horowitz Metzger (H.M.) [27].

Coats-Redfern method:

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^2} \right] = \log \frac{ZR}{Eq} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303R} \frac{1}{T} \quad (1)$$

MacCallum-Tanner method :

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{1-n} \right] = \log \frac{ZE}{Rq} - 0.485 E^{0.435} - \frac{0.449 + 0.217 E \cdot 10^3}{T} \quad (2)$$

Horowitz-Metzger method:

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{1-n} \right] = \log \frac{ZRT_s^2}{Eq} - \frac{E}{2.303RT_s} + \frac{E\theta}{2.303RT_s^2} \quad (3)$$

The frequency factor (Z) was calculated by,

$$\text{Intercept} = \log(ZR/qE)$$

and the equation used for calculating entropy change (ΔS) is

$$\Delta S = 2.303 R \log(Zh/kT_s)$$

Where, the terms have their usual meaning. Using the computer Microsoft Excel programme the linear plots of the left-hand side of eqs. (1) and (2) versus $1/T$ and against $\theta = (T - T_s)$ for eqn. (3) were drawn by the method of least squares for different values of 'n' (order of reaction) ranging from 0 to 3 in increment of 0.01 and the corresponding correlation coefficients were evaluated. The highest value of correlation coefficient gave the correct value of 'n'. From the slope and intercept, E and Z values were calculated. Using E and Z values, the values of ΔS and ΔG were determined.

The values of n, E, Z, ΔS and G estimated by all the three methods are in good mutual agreement Table-3. The value of E is sufficiently high and is comparable with other observations [28].

Table 3: Kinetic parameters derived from thermal analysis.

Complex	Method	n	E KJ/mole	Z S ⁻¹	ΔS J/K/mole	G KJ/mole
[C ₃₀ H ₂₈ N ₂ O ₈ Ni]	C.R	0.65	143.4418	9.95x10 ¹⁰	-40.6402	146.5358
	M.T	0.65	146.2568	1.54x10 ¹³	-1.272462	146.1600
	H.M	0.95	167.2607	9.62x10 ¹³	-16.51955	166.0031
[C ₂₈ H ₂₂ Br ₂ N ₂ O ₆ Ni]	C.R	1.1	127.3132	5.61x10 ⁰⁹	-64.4191	132.1401
	M.T	1.1	129.9296	6.56x10 ¹¹	-24.8185	131.7892
	H.M	1.2	152.3562	3.45x10 ¹⁶	-65.5758	147.4426

X- Ray Diffraction

The complexes of L6 and L8 were used to study the X-ray powder diffractogram as a representative system. The X-ray diffraction pattern of the complexes with respect to their prominent peaks has been indexed by using computer software [29]. The observed 2θ with relative intensity more than 10% are indexed and have been used for evaluation. The complex of ligand L6 have 8 reflections of 2θ between 5 to 80 with maximum $2\theta = 12.196$ and $d = 7.254 \text{ \AA}$ are observed. The above index method also yielded miller indices (h, k, l) values, unit cell parameters, volume of unit cell and space group. The unit cell parameters for the given diffractogram are $a = 11.65607 \text{ \AA}$, $b = 34.02341 \text{ \AA}$ and $c = 7.31117 \text{ \AA}$ and unit cell volume $V = 2476 \text{ \AA}^3$ with $\alpha = \gamma = 90.00^\circ$ and $\beta = 121.32^\circ$. The complex of ligand L8 have 11 reflections with maximum $2\theta = 11.795$ and $d = 7.496 \text{ \AA}$ are observed. The unit cell parameters for the given diffractogram are $a = 19.92965 \text{ \AA}$, $b = 9.35182 \text{ \AA}$, $c = 12.58909 \text{ \AA}$ and unit cell volume $V = 1932 \text{ \AA}^3$ with $\alpha = \gamma = 90.00^\circ$ and $\beta = 124.57^\circ$. The experimental density value of the complex was determined by using

specific gravity method [30]. The observed density for $[\text{Ni}(\text{L6})_2]$ and $[\text{Ni}(\text{L8})_2]$ is 1.202 g cm^{-3} and 1.781 g cm^{-3} while calculated density from Z value and unit cell volume for complexes are 1.2695 g cm^{-3} and 1.8242 g cm^{-3} respectively. The porosity percentage calculated from the observed and calculated densities was found to be 5.321 and 7.832 respectively. The particle size of complexes [31] was found to 115.657 and 113.457 Å respectively for the complexes of L6 and L8. The number of molecules (n) per unit cell were calculated using equation $\rho = nM/NV$. Both the crystal system was found to be monoclinic with 4 molecules per unit cell.

Fungicidal Activity

The ligand and their metal chelates were screened by mycelial dry weight (MDW) method in vitro against *Aspergillus niger* for their fungicidal activity in glucose nitrate (GN) media. Medium prepared by adding 10gm of Glucose, 2.5gm of KNO_3 , 1gm of KH_2PO_4 and 0.5gm of MgSO_4 in 1 liter of distilled water and the fungus was cultivated on GN media. The ligand and complexes under investigation were added to GN medium preparing solutions/suspension (200 ppm and 400 ppm). The conical flask containing medium with ligand and complexes, autoclaved at 15 lbs for 30 min., inoculated with *A. niger*, after 168 hours the mycelium obtained was collected by filtration through Whatman filter paper. The yield of MDW was recorded. The ligand exhibited toxicity in the inhibition. Due to synergistic combination of the coordinated metal ions with the ligands, the inhibition has been increased in complexes by 80 to 100%. The results obtained are shown in Table 4. The results are similar to the observations made by other workers [10, 11].

Table 4: Yield of Mycelial Dry Weight (MDW) in mg. at 200ppm and 400ppm for ligand and their metal complexes after 168 hrs.

Ligand	MDW in mg. of Ligand (% inhibition)		MDW in mg. of Complex (% inhibition)	
	200 ppm	400 ppm	200 ppm	400 ppm
Control	88	88	88	88
L1	65 (26.13)	30 (65.90)	20 (77.27)	23 (73.86)
L2	67 (23.86)	32 (63.63)	23 (73.86)	21 (76.13)
L3	75 (14.77)	36 (59.09)	46 (47.72)	24 (72.72)
L4	70 (20.45)	36 (59.09)	44 (50)	18 (79.54)
L5	61 (30.68)	28 (68.18)	42 (52.27)	01 (98.86)
L6	54 (38.63)	26 (70.45)	46 (47.72)	12 (86.36)
L7	40 (54.54)	19 (78.40)	29 (67.04)	08 (90.90)
L8	58 (34.09)	28 (68.18)	57 (35.22)	01 (98.86)

CONCLUSIONS

From the above discussion, we proposed square planer geometry for the Ni^{II} complexes (Fig.2). The ligand behaves as ON bidentate coordinating through azomethine nitrogen and oxygen of enolic carbonyl group. The complexes are biologically active since they exhibit enhanced antifungal activities compared to their parent ligands. The thermal study of complexes indicates that they are thermally stable. The XRD study suggests monoclinic crystal system.

Ligand	X	Y	Z
L1	Cl	H	H
L2	OH	H	H
L3	OCH ₃	H	H
L4	CH ₃	H	H
L5	Br	H	H
L6	COOH	H	H
L7	H	O-CH ₂ -CH ₃	H
L8	Cl	H	Cl

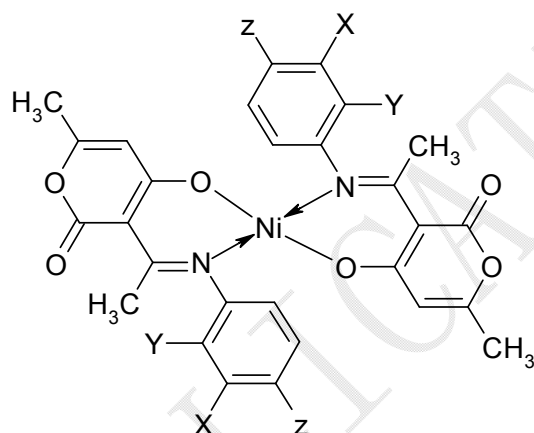


Fig.2 : The Proposed structure of Ni^{II} complex.

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