

Synthesis and spectroscopic characterization of nickel(ii) complexes with salicyldehyde semicarbazone (L₁) and 4-hydroxy acetophenone semicarbazone(L₂)

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ABSTRACT

New Ni(II) complexes containing ligands Salicyldehyde semicarbazone (L₁), and 4-hydroxy acetophenone semicarbazone(L₂), have been synthesised. The ligands were characterised on the basis of elemental analyses, IR, ¹H NMR and mass spectral studies and all the complexes were characterised by elemental analyses, molar conductance, magnetic moment, IR, electronic spectral studies. The IR spectral data for ligand L₁ indicated that the involvement of phenolic oxygen, oxygen from (–C=O) group and azomethine nitrogen in coordination with, (L₁) in coordination to the central metal ion act as tridentate ligand and involvement of oxygen from (–C=O) group and azomethine nitrogen with (L₂) in coordination to the central metal ion act as bidentate ligand. On the basis of elemental analyses and molar conductance data the complexes were found to have general composition [Ni(L₁)(X)(H₂O)₂] and [Ni(L₂)₂X₂] [(where L=L₁, and L₂, X = Cl⁻, NO₃⁻]. On the basis of IR, electronic and EPR spectra of complexes, distorted octahedral geometry has been assigned for all the complexes were found with planar coordination of the ligand around Ni⁺⁺ ion and the anions occupies axial position.

Keywords: Salicyldehyde semicarbazone(L₁), 4-hydroxyacetophenone semicarbazone(L₂), Ni(II) complexes, spectral studies.

1. INTRODUCTION

Schiff's bases such as thiosemicarbazones and semicarbazones are important class of compounds which have long attracted attention, owing to their remarkable biological and pharmacological properties [1]. Semicarbazones present a wide range of bioactivities, and their chemistry and pharmacological applications have been extensively investigated. The biological properties of semicarbazones are often related to metal ion coordination. There has been considerable interest in the studies of semicarbazones due to their unusual coordination modes when bound to metals [2]. The orally administered drug naftazone (1,2-naphthoquinone semicarbazone) protects the vascular system through an inhibitory effect on nitric oxide synthesis [3]. Many other bioactivities of semicarbazones have been reported, such as their antimicrobial [4], pesticide [5], herbicide [6] and hypnotic [7], properties or the ability of some of their Cu(II) complexes to mimic superoxide

dismutase activity [8]. Semicarbazones are widely used as spectrophotometric agents for the analysis of metal ions [9]. Semicarbazones are frequently used in the qualitative organic analysis of carbonyl compounds [10]. A large number of authors were interested in investigating the biological and medicinal properties of transition metal complexes of semicarbazones in recent years.

In view of above applications it is highly desirable to synthesize and characterize transition metal complexes with such ligands (Figure 1). In the present paper we report the synthesis, and spectroscopic characterization of Ni(II) complexes with ligand Salicyldehyde semicarbazone (L₁) and 4-hydroxy acetophenone semicarbazone (L₂) of the type [Ni(L₁)(X)(H₂O)₂] and [Ni(L₂)₂X₂] [(where L=L₁, and L₂, X = Cl⁻, and NO₃⁻]

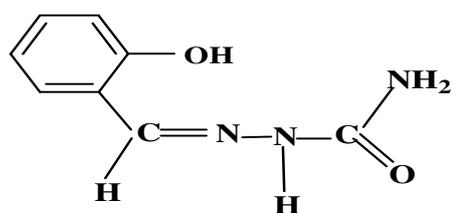
2. EXPERIMENTAL

2.1. Materials

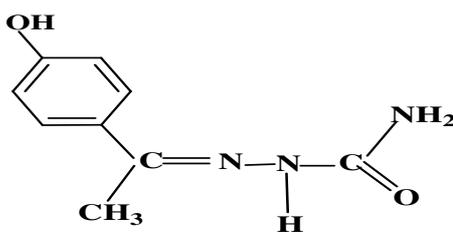
The entire chemical used were of analytical reagent and procured from sigma Aldrich and used without further purification. Metal salts were purchased from E.Merck and were used as received.

2.2. Physicochemical Measurements

The C, H, and N were analyzed on Carlo-Erba 1106 elemental analyzer. IR Spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. Molar conductance was measured at 25°C on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using CuSO₄·5H₂O as calibrant. Electronic impact mass spectrum was recorded on JEOL, JMS - DX-303 mass spectrophotometer. Proton (1H) NMR spectra were recorded on JEOL -DELTA 2 NMR model ECX 400P spectrometer using DMSO as a solvent. Chemical shifts are given in ppm relative to tetramethylesilane(TMS) The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer.



[Str.1]



[Str.2]

Figure - 1: Structure of ligand L₁ and L₂

2.3. Synthesis of ligands and Cu(II) complexes

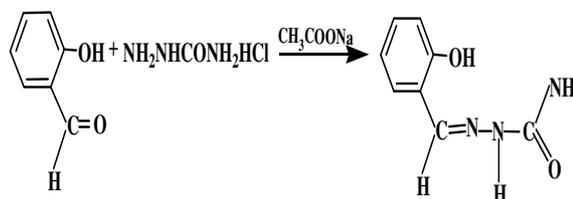
2.3.1. Synthesis of ligands

Both the ligands were prepared by reported method.

2.3.1.1. Synthesis of ligand L₁

An aqueous solution of semicarbazide hydrochloride (2.22 g, 0.02mol) and salicylaldehyde (2.10mL, 0.02 mol) were mixed slowly in the

presence of anhydrous sodium acetate (1.64 g, 0.02mol). This mixture was stirred vigorously with the help of mechanical stirrer for an hour. On cooling a white product or compound was precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P₄O₁₀. The structure of ligand and method of synthesis is shown below in the scheme 1.

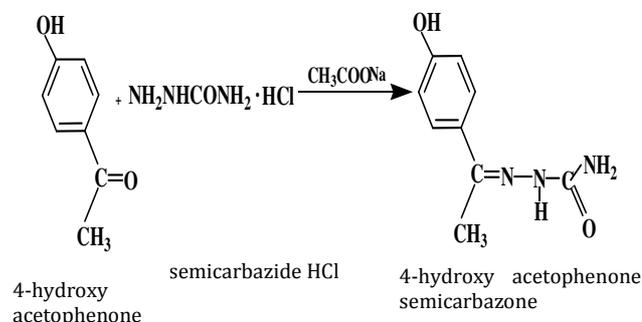


semicarbazide salicylaldehyde HCl Semicarbazone(L₁)

Scheme - 1: Preparation of ligand L₁

2.3.2. Synthesis of ligand L₂

An aqueous solution of semicarbazide hydrochloride (2.22 g, 0.02mol) and 4-hydroxy acetophenone (2.44mL, 0.02mol) were mixed slowly in the presence of anhydrous sodium acetate (1.64 g, 0.02mol). This mixture was stirred vigorously with the help of mechanical stirrer for an hour. On cooling a white product or compound were precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P₄O₁₀. The structure of ligand and method of synthesis is shown below in the scheme 2.



Scheme - 2: Preparation of ligand L₁

2.3.3. Preparation of the Ni(II) complexes with ligands L₁, and L₂

The complexes with ligand L₁, and L₂, were prepared by mixing the hot ethanolic solution (15mL) of the respective nickel(II) salt (0.001 mol) and an ethanolic solution (15mL) of corresponding ligand (0.001 mol) in 1:1 molar ratio in case of L₁ and 1:2 molar ratio in case L₂, were mixed together with constant stirring. This mixture was refluxed for 5- 6 hrs at 90-95 °C. On cooling colored precipitate was formed. It was filtered, washed with cold EtOH and distilled with water, and dried under vacuum over P₄O₁₀. The purity of complexes was checked by using thin layer chromatography (TLC). The preparation of

complexes can be represented by the following general equations:

Schiff base Ligand (L) + nickel salt \rightarrow colored complex

3. RESULTS AND DISCUSSION

3.1 Characterization of the nickel(II) complexes

The analytical and physical properties of prepared complexes are given in table 1. The reported nickel(II) complexes provide satisfactory C, H, N, and Ni analyses and confirmed the general composition of $[\text{Ni}(\text{L}_1)(\text{X})(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{L}_2)_2\text{X}_2]$ with ligand L_1 and L_2 respectively (where $\text{L}=\text{L}_1$, and L_2 , $\text{X} = \text{Cl}^-$, and NO_3^-). The isolated solid complexes are stable in air.

3.2 Conductivity studies

All the complexes have shown good solubility in DMSO. The molar conductance of the complexes in fresh solution of DMSO lies in the range of $17-21\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their non-electrolytic behavior. Thus, the complexes may be formulated as $[\text{Ni}(\text{L}_1)(\text{X})(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{L}_2)_2\text{X}_2]$ for ligand L_1 and L_2 respectively. (where $\text{L}_1 =$ Salicyldehyde semicarbazone, and $\text{L}_2 =$ 4-hydroxy acetophenone semicarbazone, $\text{X} = \text{Cl}^-$, and NO_3^-) (Table 1)

3.3. Magnetic susceptibility measurements

All the complexes of Ni(II) show magnetic moment in the range 2.86-3.00 B. M. (Table 1) corresponding to two unpaired electrons [11]. It indicates that these complexes may have six coordinated octahedral geometry. However, it is quite difficult to assign the geometry only on the basis of magnetic moment. The possible geometry will be elucidated on the basis of electronic spectral studies

3.4. Spectroscopic characterization

3.4.1. Infrared spectra

The assignments of the significant IR spectral bands ($4000-400\text{cm}^{-1}$) of ligand and its metal complexes are presented in table 2. An interesting attribute of the semicarbazones is that in the solid state, they predominantly exist in the keto form, whereas in solution state, they exhibit a keto-enol tautomerism. The position of bands provides significant indications regarding the bonding sites of the ligand molecule when complexed with Ni(II). The IR spectra of L_1 shows $\nu(\text{-NH})$ band at 3320cm^{-1} is present, indicating that in the solid state, the ligand remains as the keto form. The position of $\nu(\text{C=N})$ band of the ligand (L_1) and L_2 appeared at 1623cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via the azomethine

nitrogen [12,13]. This is also confirmed by the appearance of bands in the range of $451-512\text{cm}^{-1}$, this has been assigned to the $\nu(\text{M-N})$ [14]. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethine nitrogen. The position of $\nu(\text{-OH})$ band of the (L_1) appeared at 3494cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via oxygen of phenolic group. The band appearing at $1700-1708\text{cm}^{-1}$ corresponding to $\nu(\text{C=O})$ in the IR spectrum of ligand is shifted towards lower wave number (Figure 2). It indicates that oxygen of (C=O) group coordinates to the metal ion [15,16]. Thus, it may be concluded that the ligand behaves as tridentate chelating agent coordinating through phenolic oxygen, azomethine nitrogen and keto oxygen. But with ligand L_2 the (-OH) band of phenolic group remain intact at their position, which indicated that it is not coordinating on complexation with metal ion. So ligand L_2 behave as bidentate.

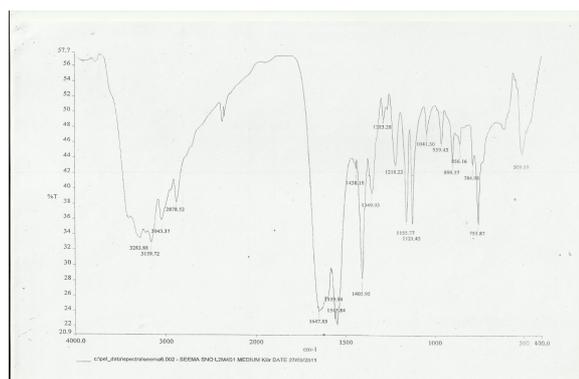


Figure - 2a: IR Spectra of $[\text{Ni}(\text{L}_1)(\text{Cl})(\text{H}_2\text{O})_2]$

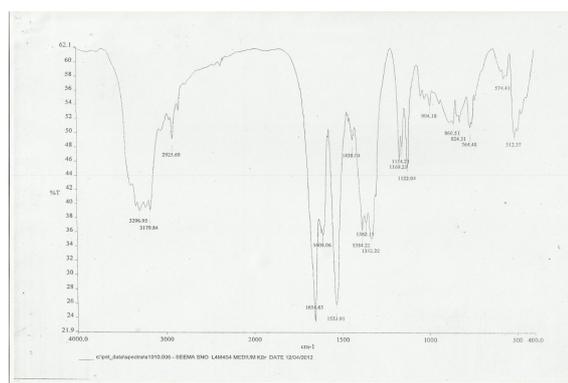


Figure - 2b: IR spectra of $[\text{Ni}(\text{L}_2)_2(\text{NO}_3)_2]$

3.4.2. Bands due to anions

The coordination modes of nitrate anion in nitrate complexes show three vibrational bands at $1482-1426$, $1328-1311$ and $1050-1031\text{cm}^{-1}$. The separation of the two highest frequency is more than 90cm^{-1} , indicating the unidentate

Table - 1: Physical properties, elemental analysis, magnetic moment and molar conductance data of Ni(II) complexes with ligand L₁ and L₂

Complexes	Molar conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Color	m.p ($^{\circ}\text{C}$)	Yeild (%)	Elemental Analysis data found /(calculated)%				μ_{eff} (B.M)
					Ni	C	H	N	
L ₁ (C ₈ H ₉ N ₃ O ₂)	-	White	200- 202	69	-	53.62 (53.63)	5.05 (5.03)	23.48 (23.46)	-
[Ni(L ₁)(Cl)(H ₂ O) ₂] NiC ₈ H ₁₃ N ₃ O ₄ Cl	19	Green	250	58	18.83 (18.80)	31.14 (31.11)	4.23 (4.21)	13.63 (13.61)	2.88
[Ni(L ₁)(NO ₃)(H ₂ O) ₂] NiC ₈ H ₁₃ N ₄ O ₇	18	Green	280	66	17.34 (17.31)	28.68 (28.65)	3.90 (3.88)	16.72 (16.71)	2.86
L ₂ C ₉ H ₁₁ N ₃ O ₂	-	Cream white	232- 235	65	-	55.99 (55.96)	5.73 (5.70)	21.78 (21.76)	-
[Ni(L ₂) ₂ Cl ₂] NiC ₁₈ H ₂₂ N ₆ O ₄ Cl ₂	21	Sea Green	245	65	11.04 (11.00)	41.92 (41.94)	4.25 (4.27)	16.29 (16.31)	2.94
[Ni(L ₂) ₂ (NO ₃) ₂] NiC ₁₈ H ₂₂ N ₈ O ₁₀	17	Sea Green	288	64	10.22 (10.21)	38.00 (38.02)	3.86 (3.87)	19.71 (19.72)	3.00

Table - 2: Important IR spectral bands (cm⁻¹) of ligands and Ni(II) complexes

Complexes	$\nu(-\text{OH}) +$	$\nu(-\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{X})$ X= Cl ⁻ , NO ₃ ⁻
Ligand (L ₁)	3494,3278		1623	1700	-	-
[Ni(L ₁)(Cl)(H ₂ O) ₂]	3283,3159		1559	1647	509	360
[Ni(L ₁)(NO ₃)(H ₂ O) ₂]	3394,3253		1600	1672	499	1482,1311,1031
Ligand (L ₂)	3509,3320		1623	1708	-	-
[Ni (L ₂) ₂ Cl ₂]	3247		1549	1642	451	336
Ni(L ₂) ₂ (NO ₃) ₂]	3179		1608	1654	512	1426,1328,1050

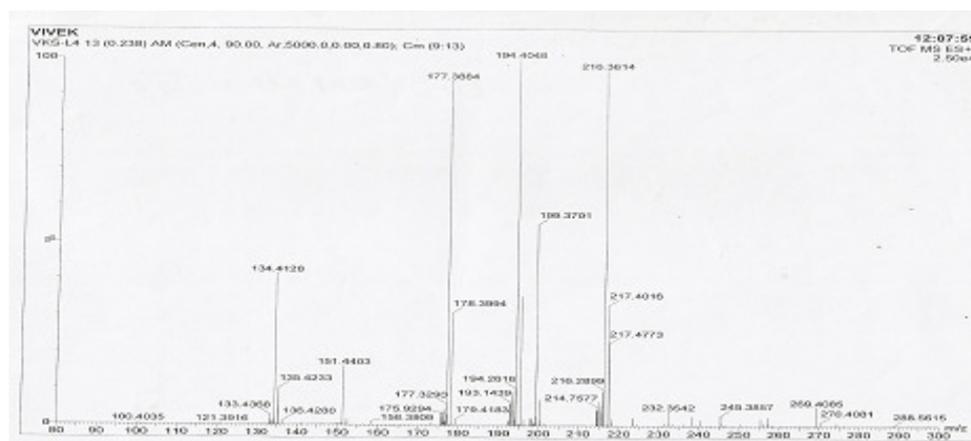


Figure - 3: Mass spectra of ligand L₂

coordination [17-18]. In the IR spectra of Ni(II) chloride complexes, bands corresponding to $\nu(\text{Ni}-\text{Cl})$ observed at 336-360 cm^{-1} indicating the presence of M-Cl bond and In the IR spectra of Ni(II) complexes with ligand L₁, also show a clear band of water molecule at 645-655 cm^{-1} ,

indicating that water molecule is also coordinating with ligand L₁ [19].

3.4.3. Electronic spectra

Electronic spectra of six coordinated Ni(II) complexes may possess O_h or D_{4h} symmetry. From the Orgel energy level diagram for

octahedral complexes the three spin allowed transition should be observed. The electronic spectra of complexes $[\text{Ni}(\text{L})_2\text{X}_2]$ (where $\text{L} = \text{L}_1$ and L_2 , $\text{X} = \text{Cl}^-$, and NO_3^-) show three bands in the range of 10537-10193, 10764-18621 and 22554-32120 cm^{-1} assignable to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) transition respectively^[20]. There is splitting of (ν_1) band, which is generally observed in D_{4h} symmetry. Thus complexes, under study possess the distorted octahedral geometry.

3.4.4. Electronic ${}^1\text{H}$ NMR spectra of ligand

${}^1\text{H}$ NMR spectrum of Ligands in DMSO show the signals^[21] as follows (chemical shift in ppm): ${}^1\text{H}$ NMR spectrum of Ligand L_1 (Salicyldehyde semicarbazone), : δ : 3.4 ppm (s) (2H, $\text{H}_2\text{N}-\text{C}=\text{O}$), δ : 7.7 ppm (s) (1H, $\text{HN}-\text{C}=\text{O}$), δ : 6.9 ppm (m) (4H, -Ph-), δ : 9.9 ppm (s) ($\text{H}_3\text{C}=\text{N}$), δ : 10.23 ppm (s) (Ph-OH), and ${}^1\text{H}$ NMR spectrum of Ligand L_2 (4-hydroxy acetophenone semicarbazone),: δ : 3.3 ppm (s) (2H, $\text{H}_2\text{N}-\text{C}=\text{O}$), δ : 7.4 ppm (s) (1H, $\text{HN}-\text{C}=\text{O}$), δ : 6.7 ppm (s) (1H, -Ph-), δ : 9.6 ppm (s) ($\text{H}_3\text{C}=\text{N}$), δ : 11.37 ppm (s) (-Ph-OH), δ : 2.1 ppm (t) (3H), ($\text{H}_3\text{C}-\text{C}$).

3.4.5. Mass spectra

The electronic impact mass spectrum of the ligand L_1 shows a molecular ion (M^{+1}) peak at $m/z = 179$ amu corresponding to species $[\text{C}_8\text{H}_9\text{N}_3\text{O}_2]^+$, which confirms the proposed formula. It also shows a series of peaks corresponding to species $[\text{C}_8\text{H}_9\text{N}_3\text{O}]^+$ i.e at 163 amu and various fragments at 135, 120, 91 amu. The electronic impact mass spectrum of the ligand L_2 (Figure 3) a molecular ion (M^+) peak at $m/z = 193$ amu corresponding to species $[\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2]^+$, which confirms the proposed formula. It also shows a series of peaks corresponding to species $[\text{C}_9\text{H}_{11}\text{N}_3\text{O}]^+$ i.e at 177 amu and various fragments at 134, 120 and 93 amu. Intensity of these peaks give an idea of the stability of the fragments. Figure 3.

4.5. Ligand field parameters

The ligand field parameters were calculated and are listed in table 3. Dq value have been calculated from the transition energy ratio diagram^[22]. The value of B for a given complex can be calculated as :

$$B = (\nu_1 + \nu_2 - 3\nu_3)/15$$

The value of Racah parameter B found in complexes are less than the value of 1041cm^{-1} . The value of Dq found in octahedral complexes of Ni(II) vary between $968-1089\text{cm}^{-1}$ depending on

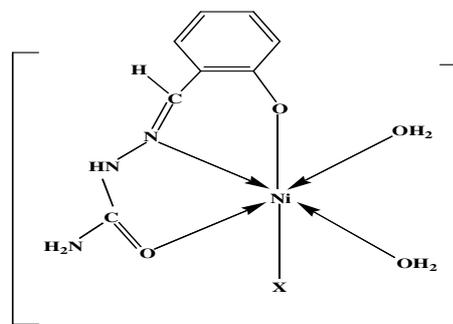
the position of the ligand in the spectrochemical series. The β is defined as:

$$\beta = B(\text{complex}) / B(\text{free ion})$$

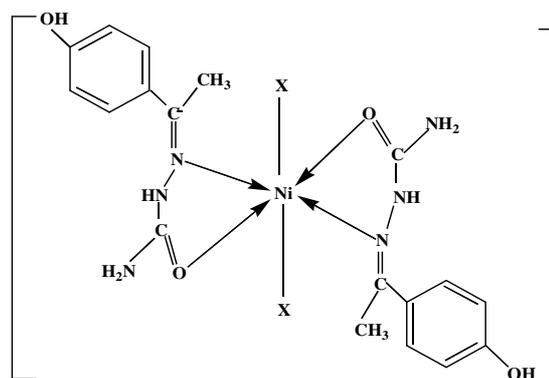
Where B (free ion) for Ni (II) is 1041cm^{-1} ^[23]. The value of β lies in the range of 0.61-0.92. These values indicate the covalent character in the metal-ligand bond.

Table - 3: Ligand Field Parameters of Ni(II) Complexes with ligand L_1 and L_2

Complexes	Dq cm^{-1}	B cm^{-1}	B	LFSE (KJmol^{-1})
$[\text{Ni}(\text{L}_1)\text{Cl}(\text{H}_2\text{O})_2]$	1019	911	0.87	146
$[\text{Ni}(\text{L}_1)(\text{NO}_3)(\text{H}_2\text{O})_2]$	1037	689	0.66	148
$[\text{Ni}(\text{L}_2)_2\text{Cl}_2]$	1023	738	0.70	146
$[\text{Ni}(\text{L}_2)_2(\text{NO}_3)_2]$	1039	930	0.89	149



A



B

Figure - 4: [A] proposed Structure of the Ni(II) complexes with ligand L_1 , Salicyldehyde semicarbazone, (where $\text{X} = \text{Cl}^-$, NO_3^-); [B] proposed Structure of the Ni(II) complexes with ligand L_2 , 4-hydroxyacetophenone semicarbazone) (where $\text{X} = \text{Cl}^-$, NO_3^-)

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