

Studies of Some Transition Metal Complexes with β -Hydroxy α -Naphthalidine Anthranilino Hydroxamic Acid

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A series of complexes of the type MLX_3 [$M = Co(II), Cu(II)$ and $Ni(II)$, $X = H_2O$, pyridine, and α, β or γ picolines] have been synthesized with the ligand β -hydroxy α -naphthalidine anthranilino hydroxamic acid, H_2L . Characterization of the ligand as well as complexes have been done on the basis of elemental analysis, spectral studies and conductivity and magnetic susceptibility measurements. Ligand has been found to coordinate through two of its nitrogen and one oxygen atoms. The complexes are found to be octahedral, the remaining three coordination sites are satisfied by oxygen of H_2O or nitrogen of nitrogen donors such as pyridine and α, β or γ picolines.

INTRODUCTION

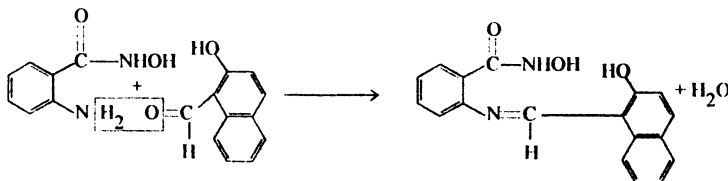
Much work has been done on metal complexes with hydroxamic acid and their derivatives as ligands¹⁻¹⁰ but little attention seems to have been given on mixed ligand complexes. Therefore, in the present investigation, we report here a series of complexes of $Co(II)$, $Ni(II)$ and $Cu(II)$ of the type MLX_3 .

EXPERIMENTAL

All the chemicals used in the present study were from BDH of reagent grade. The β -hydroxy α -naphthaldehyde and 2-amino benzhydroxamic acid obtained from Aldrich (USA) were used without further purification.

Preparation of the ligand

The ligand has been prepared by the condensation of β -hydroxy α -naphthaldehyde with anthranilino hydroxamic acid in aqueous alcoholic medium at reflux temperature.



Equimolar amount of sodium salt of anthranilino hydroxamic acid dissolved in glacial acetic acid was mixed with β -hydroxy- α -naphthaldehyde dissolved in minimum volume of ethanol. The mixture was stirred vigorously till a brownish yellow precipitate appeared. This was then refluxed for 1/2 h. A clear deep brownish-yellow solution was obtained which on cooling gave brownish-yellow solution crystals of ligand. The compound was filtered, washed with cold water

and a little alcohol and then recrystallised with alcohol. The filtrate after cooling gave another crop of a base which was filtered out. The compound is easily soluble in acetone, less soluble in cold ethanol but more soluble in hot ethanol.

The compound was further analysed and found to contain C = 70.5%, H = 4.52%, N = 9.10% which corresponds with the molecular formula $C_{18}H_{14}N_2O_3$.

Preparation of the complexes

The corresponding metal acetate was dissolved in aqueous ethanolic solution. The ligand solution in ethanol was added to it. The metal ligand molar ratio was kept as 1 : 1. The whole solution was then refluxed for 1–2 h till the complexes separated out. The precipitate thus obtained was filtered, washed with ethanol water and dried over KOH in a desiccator. Acetates of Co(II), Ni(II) and Cu(II) used separately and the complexes with each metal were prepared with ligand in aqueous medium and in the presence of bases like pyridine, α -picoline, β -picoline and γ -picoline.

On the basis of analytical data [Table-1], the complexes were found to possess the composition MLX_3 , where M = Co(II), Ni(II) and Cu(II) and X = H_2O , pyridine, α -picoline, β -picoline or γ -picoline.

Copper was estimated iodometrically. Nickel and cobalt were estimated gravimetrically as bis-dimethyl glyoximato nickel(II) and $CoSO_4$ respectively. C, H and N were estimated by semimicro-combustion method.

Electrical conductivity of solutions of complexes was measured by conductivity meter bridge manufactured by Wiss-Techen Werch Staten type-LBR at room temperature in DMF. The cell constant was measured (at room temperature $30^\circ C$) using N/10 and N/100 KCl solutions. Pure DMF and conductivity water were used as solvents. The electronic absorption spectra of the complexes were recorded with Hitachi-320 spectrophotometer at CDRI, Lucknow. The infrared spectra were recorded on Perkin-Elmer 577 spectrophotometer using KBr pellets in the range of $4000-400\text{ cm}^{-1}$ at CDRI, Lucknow. Magnetic susceptibilities of the complexes were determined by Gouy's method.

The ligand, β -hydroxy α -naphthalidine anthranilino hydroxamic acid, can exist in keto-enol tautomeric forms. The probable tautomeric structures would be as shown below:

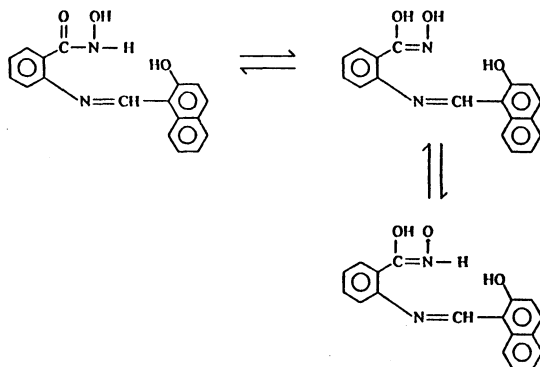


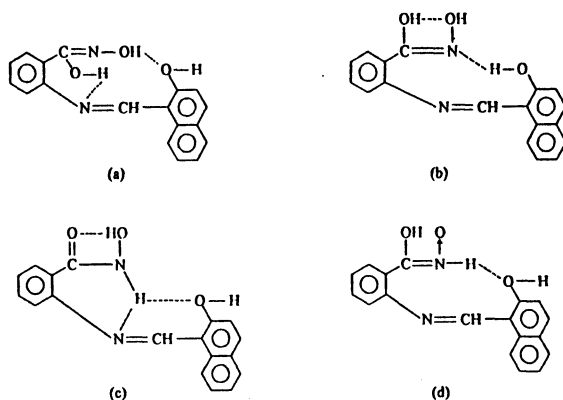
TABLE-1
ANALYTICAL DATA OF THE COMPLEXES OF Co(II), Ni(II) AND Cu(II)
IONS WITH β -HYDROXY α -NAPHTHALDEHYDE ANTHRANILINO
HYDROXAMIC ACID [MLX₃]

Complexes	% Analysis, Found (Calcd.)			
	M	C	H	N
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	14.96 (15.06)	51.15 (51.30)	4.10 (4.27)	6.55 (6.64)
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(C ₅ H ₅ N) ₃	10.40 (10.50)	65.40 (65.50)	4.41 (4.46)	11.49 (11.57)
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(α -pico) ₃	9.78 (9.82)	66.75 (66.82)	5.00 (5.10)	10.76 (10.82)
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(β -pico) ₃	9.74 (9.82)	66.73 (66.82)	4.95 (5.10)	10.73 (10.82)
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(γ -pico) ₃	9.75 (9.82)	66.74 (66.82)	4.98 (5.10)	10.75 (10.82)
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	14.00 (14.08)	57.80 (57.83)	4.25 (4.31)	6.68 (6.71)
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(C ₅ H ₅ N) ₃	9.68 (9.78)	66.00 (66.03)	4.45 (4.50)	11.58 (11.67)
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(α -pico) ₃	9.02 (9.14)	67.28 (67.32)	5.00 (5.14)	10.85 (10.90)
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(β -pico) ₃	9.00 (9.14)	67.20 (67.32)	5.03 (5.14)	10.80 (10.90)
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(γ -pico) ₃	8.95 (9.14)	67.24 (67.32)	5.00 (5.14)	10.88 (10.90)
Co(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	14.00 (14.13)	51.75 (51.80)	4.28 (4.31)	6.65 (6.71)
Co(C ₁₈ H ₁₂ N ₂ O ₃)(C ₅ H ₅ N) ₃	9.75 (9.82)	65.85 (66.00)	4.45 (4.50)	11.60 (11.66)
Co(C ₁₈ H ₁₂ N ₂ O ₃)(α -pico) ₃	8.95 (9.18)	67.18 (67.29)	5.00 (5.14)	10.78 (10.90)
Co(C ₁₈ H ₁₂ N ₂ O ₃)(β -pico) ₃	9.00 (9.18)	67.15 (67.29)	5.05 (5.14)	10.80 (10.90)
Co(C ₁₈ H ₁₂ N ₂ O ₃)(γ -pico) ₃	8.98 (9.18)	67.15 (67.29)	4.98 (5.14)	10.82 (10.90)

TABLE-2
IR DATA (cm⁻¹) OF THE LIGAND AND THE COMPLEXES OF THE TYPE MLX₃

Ligands	Amide I		Amide II		1200m	1080m	960-410
	3260s	166s	1480s	1365s			
	v(OH) + v(NH)	v(C=N) + v(C=O)	v(C-N) + v(NH)	v(C-O) phenolic	v(OH) deformation	v(N-O)	phenyl ring + hydroxamic acid part deformation vibrations
Complexes	v(OH)	v(C=N)	v(C=O) phenolic			v(N-O)	
Co(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	3400s	1590s	1530m			1180m, 1150m	
Co(C ₁₈ H ₁₂ N ₂ O ₃)(C ₃ H ₅ N) ₃	3400s	1590s	1530m			1180m	
Co(C ₁₈ H ₁₂ N ₂ O ₃)(α-pico) ₃	3400s	1590s	1535m			1180m, 1155m	
Co(C ₁₈ H ₁₂ N ₂ O ₃)(β-pico) ₃	3400s	1590s	1535m			1180m	
Co(C ₁₈ H ₁₂ N ₂ O ₃)(γ-pico) ₃	3400s	1590s	1535m			1180m, 1160m	
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	3400s	1600s	1540m			1180m	
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(C ₃ H ₅ N) ₃	3400s	1585s	1535m			1180m	
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(α-pico) ₃	3400s	1590s	1535m			1180m, 1160m	
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(β-pico) ₃	3400s	1600s	1540m			1180m	
Ni(C ₁₈ H ₁₂ N ₂ O ₃)(γ-pico) ₃	3400s	1600s	1540m			1180m	
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(H ₂ O) ₃	3400s	1600s	1535m			1180m, 1160m	
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(C ₃ H ₅ N) ₃	3400s	1600s	1530m			1180m, 1155m	
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(α-pico) ₃	3400s	1600s	1535m			1180m	
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(β-pico) ₃	3400s	1600s	1530m			1180m	
Cu(C ₁₈ H ₁₂ N ₂ O ₃)(γ-pico) ₃	3400s	1600s	1530m			1180m	

In the above tautomeric forms there is a probability of strong hydrogen bond forming tendency for phenolic —OH and oxime —OH groups as shown below:

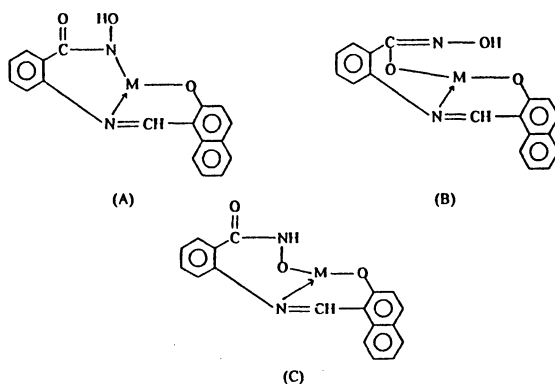


Due to the various ways of the formation of hydrogen bond, it is expected that $\nu(\text{OH})$ frequency of the ligand molecule sharply falls below the expected range of $\nu(\text{OH})$ vibration.

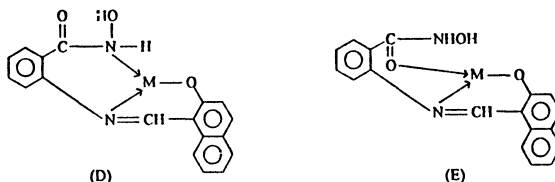
The IR spectrum of this ligand H_2L [Table-2] has been recorded in KBr disc. The ligand displays highest IR band at 3260 cm^{-1} which may be attributed to combined $\nu(\text{OH})$ and $\nu(\text{NH})$ frequencies. The $\nu(\text{OH})$ of the enol form ($\text{C}-\text{OH}$) shifts from $3500-3260\text{ cm}^{-1}$ due to strong hydrogen bonding. In some complexes $\nu(\text{OH})$ vibration has been located around 3400 cm^{-1} indicating that strong hydrogen bonding present in the ligand molecule has been broken down and at least one free —OH group exists even after coordination. The ligand displays a medium amide-I band at 1665 cm^{-1} and the band is attributed mainly due to $\nu(\text{C}=\text{N})$ while that at 1480 cm^{-1} may be assigned as amide II ($\nu(\text{OH}) + \delta(\text{OH})$). The hydroxamic acid part ($\text{N}-\text{O}$) is attributed to sharp band located at 1080 cm^{-1} . The phenolic group $\nu(\text{OH})$ bending mode of vibration is located at 1210 cm^{-1} and this is affected appreciably in complexes and in almost all complexes it disappears.

The ligand has different donor sites and it can form chelate ring in various ways. The probable mode of bonding forms of the ligand molecule are shown below:

As Dianionic Molecule

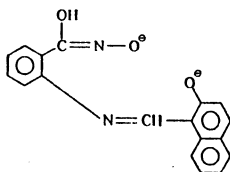


As Mono-anionic molecule



IR Spectra of the Complexes [MLX₃] (Table-3)

The Schiff base of the 2-amino benzhydroxamic acid with β -hydroxy α -naphthaldehyde is highly sensitive in the enol form. This is expected that two hydroxy (OH) protons of the ligand molecule will be deprotonated forming

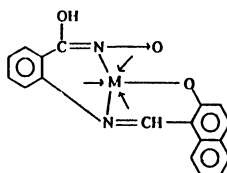


dianionic tridentate donor molecule. In this case (N—OH) proton of the hydroxamic acid moiety and second proton of the phenoxy (OH) are lost producing binegative ion. The resulting ligand acts as tridentate molecule which coordinates through deprotonated phenolic oxygen, imide nitrogen and oximo nitrogen in complexes [MLX₃].

In almost all the complexes $\nu(\text{OH})$, amide bands, $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{O})$ of the ligand molecule are affected appreciably. The strong and sharp (O—H) and (N—H) vibrations of the ligand at 3260 cm^{-1} disappear in all the complexes of the ligand and a new broad band appears in the complexes at about 3400 cm^{-1} confirming the presence of at least one free (OH) group even in the complexes. The disappearance of the strong band at 3260 cm^{-1} further suggests the deprotonation of the second (OH) group i.e. (N—OH) proton located at hydroxamic acid moiety. The amide I band located at 1665 cm^{-1} in the ligand is also shifted to lower frequency in almost all the complexes by about $65\text{--}80\text{ cm}^{-1}$. This shift of $\nu(\text{C}=\text{N})$ band towards lower frequency in the complexes suggests the coordination of the imide nitrogen of the ligand in the complexes. The medium but sharp band located at 1210 cm^{-1} in the ligand attributed from deformation vibration of phenolic (OH) disappears in all the complexes supporting the deprotonation of phenolic (OH) and coordination of phenolic oxygen to the metal atom. The $\nu(\text{C}=\text{O})$ vibration of phenolic (C—O) groups shifts to higher frequency in complexes suggesting increase of bond order of (C—O) group in complexes as noticed by earlier workers². The (N—O) band of the ligand is also shifted to higher frequency expected for coordinated (N—O) nitrogen. The (M—N) stretching vibrations appear in the lower frequency regions.

Thus from the above discussion, it is inferred that deprotonated phenolic oxygen, deprotonated hydroxamic part (N—O) nitrogen and imide (C=N) nitrogen are the bonding sites of the Schiff base β -hydroxy α -naphthaldehyde

anthranilino hydroxamic acid and the probable form of the ligand to form complexes is



which is bidentate tridentate.

In case of aquo-complexes, separate band for coordinated H_2O is not obtained as it is overlapped by $\nu(\text{OH})$ vibration. The frequencies observed in the range of $800\text{--}700\text{ cm}^{-1}$ in aquo complexes may be attributed to rocking mode of coordinated water. The pyridine and picoline complexes display bands in finger print and in far infrared region. The pyridine ring breathing modes of vibration located at $1090\text{--}940\text{ cm}^{-1}$ in complexes have been regarded as the characteristic vibrations of the coordinated pyridine and different picoline molecules. The infrared bands at $590\text{--}580\text{ cm}^{-1}$ in the complexes are also characteristic of presence of pyridine molecules in the complexes.

The room temperature magnetic moment values [Table-3] in the range of 4.85–4.92 B.M. of Co(II) complexes are higher than the spin only value due to high orbital contribution resulting from ${}^4\text{T}_{1g}$ ground state. Thus the magnetic character of the complexes, CoLX_3 corresponds to octahedral geometry.

TABLE-3
ELECTRONIC SPECTRA AND MAGNETIC MOMENT STUDIES

Complexes	Colour	$\sigma\text{-}\eta$	$\pi\text{-}\pi^*$	d-d band	$\mu_{\text{eff}}(\text{BM})$
$\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{H}_2\text{O})_3$	Golden Brown	220, 260	315	410, 460	4.84
$\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_5\text{N})_3$	Yellowish Brown	220, 260	325	460	4.92
$\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\alpha\text{-pico})_3$	Yellowish Brown	220	320	415, 460	4.86
$\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\beta\text{-pico})_3$	Yellowish Brown	220	325	410, 460	4.87
$\text{Co}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\gamma\text{-pico})_3$	Yellowish Brown	220	320	410, 460	4.93
$\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{H}_2\text{O})_3$	Deep Reddish Green	222	318	410	2.89
$\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_5\text{N})_3$	Greenish Brown	220	320	425	2.90
$\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\alpha\text{-pico})_3$	Greenish Brown	222	318	415	2.99
$\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\beta\text{-pico})_3$	Greenish Brown	220	320	410	2.98
$\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\gamma\text{-pico})_3$	Greenish Brown	222	318	415	3.00
$\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{H}_2\text{O})_3$	Green	228	262, 320	420	1.93
$\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\text{C}_5\text{H}_5\text{N})_3$	Parrot Green	225	320	400	1.92
$\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\alpha\text{-pico})_3$	Green	225	320	425	1.91
$\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\beta\text{-pico})_3$	Green	228	320	420	1.93
$\text{Cu}(\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3)(\gamma\text{-pico})_3$	Green	220	315	400	1.92

The electronic absorption spectra of the complexes [Table-3] with the ligand H_2L has been recorded in methanol. The reflectance spectra of the $CoLX_3$ complexes besides $\sigma-\eta$, $\pi-\pi^*$ electronic transition at 460 nm may assigned as due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) + CT$ band. In some cases this ν_3 band is split into two component bands, one at about 410 nm and the other at about 460 nm. The splitting of the ν_3 band may be caused due to unsymmetrical ligands resulting in the formation of complexes of lower symmetry. We could not observe other transitions at lower energies which might have been overlapped by the ligand absorption bands. The low intensity bands at lower energies may be eclipsed in the extended tail of the ligand and CT band. Thus the complexes $CoLX_3$ may be octahedral in nature.

The Ni(II) complexes $NiLX_3$ have been found to have the magnetic moment in the range of 2.91–3.10 BM which is slightly above the spin only value. We know that Ni(II) in the octahedral field has ${}^3A_{2g}$ ground state which is orbitally non-degenerate. The slight rise in the magnetic moment may be due to higher state mixing v/v spin-orbit coupling. Thus the magnetic moment values of Ni(II) complexes $NiLX_3$ suggest their octahedral nature.

The reflectance spectra of Ni(II) complexes $NiLX_3$ show one band at around 410–425 nm which may be assigned due to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions. The higher energy band near 225 nm and 320 nm may be due to $\sigma-\eta$ and $\pi-\pi^*$ transitions. The lower energy transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ are not observed. Thus on the basis of reflectance spectra, we may suggest Ni(II) complexes of the ligand L_2 to be of octahedral stereochemistry.

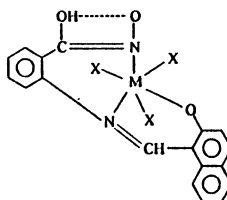
The Cu(II) complexes $CuLX_3$ are paramagnetic and the measured magnetic moment values fall around 1.91 to 1.92 BM which correspond to their distorted octahedral geometry. The reflectance spectra of the complexes $CuLX_3$ show in general broad asymmetrical band in the region 410–420 nm which may be attributed due to ${}^2B_{1g} \rightarrow {}^2E_g + CT$ band. The width and the asymmetry of the present spectral band suggest a distorted octahedral configuration in the Cu(II) complexes $CuLX_3$ which have lower symmetry than octahedral due to the presence of the mixed ligand (L and bases X) field around the central copper(II) ions.

The complexes with ligand β -hydroxy- α -naphthalidine anthranilino hydroxamic acid (BHANAHA) with the metals Co^{2+} , Ni^{2+} and Cu^{2+} are thermally stable up to 150°C without any change in colour and loss in weight which indicates that the bases like pyridine and picolines are coordinately bonded to the central metal ion. The complexes containing water molecules are resistant to heat at about 140–150°C suggesting the coordinated nature of the water molecules.

The electrical conductance shows these complexes to be non-electrolyte.

Thus keeping in view the elemental analysis, electrical conductance value, magnetic behaviour, electronic spectra, IR spectra of the complexes and bonding

sites of the ligand the probable structure MLX_3 is suggested to be octahedral in nature as shown below:



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