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Preparation and Antibacterial Activity of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Cd(II) Derived from 1-Phenylazo-2-naphthol and Salicylaldehyde

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Abstract: The mixed ligand complexes of Co(II), Ni(II), Cu(II) and Cd(II) have been synthesized by using 1-phenylazo-2-naphthol as primary ligand and salicylaldehyde as secondary ligand. All the prepared complexes were identified and confirmed by elemental analyses (C, H and N), molar conductance measurements, infrared, electronic absorption and electron paramagnetic resonance. The elemental analysis data suggest that the stoichiometry of the complexes to be 1:1:1[M: L¹: L²] ratio. The molar conductance measurements of the complexes indicate their non-electrolytic nature. The infrared spectral data showed the coordination sites of the free ligand with the central metal ion. The electronic absorption spectral data revealed the existence of an octahedral geometry for Co(II) and Cd(II) complexes and a square planar geometry for Ni(II) and Cu(II) complexes. The electron paramagnetic resonance spectra of the Co(II) and Cu(II) complexes showed the existence a paramagnetic phenomenon and supported their geometrical structures which confirmed by the electronic absorption spectra. The ligands and mixed ligand complexes have been tested on antibacterial activity against three strains of pathogenic bacteria such as *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Keywords: Mixed ligand, 1-Phenylazo-2-naphthol, Salicylaldehyde, Antibacterial activity.

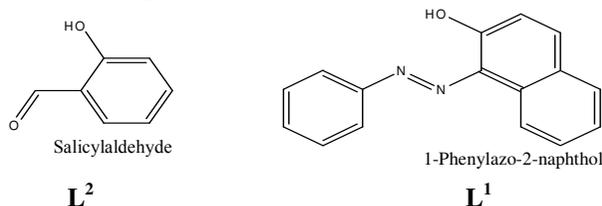
Introduction

1-Phenylazo-2-naphthol and salicylaldehyde are bidentate ligands and have a good ability to form many transition metal ion complexes¹. Some mixed ligand complexes of divalent metal

ions with salicylaldehyde, phthalic acid and *L*-alanine have been prepared and the investigation was done by using different physical techniques, in particular; elemental analysis, molar conductivity, infrared and electron paramagnetic resonance spectra². Antibacterial activity studies of the mixed ligand complexes of transition metal with maleic acid and heterocyclic amine bases have been synthesized and identified on the basis of their chemical analyses and spectral characteristics. All the complexes have been evaluated to possess octahedral structures and their biological activities³. Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 3-salicylienediazono-2-indolinone was carried out by Konstantininovic *et al.*⁴. They found that Ni(II) and Cu(II) complexes have a square planar geometry and a tetrahedral one for the Co(II) and Zn(II) complexes and were found to exhibit antibacterial activity against *Staphylococcus aureus*, *Enterococcus D*, *Proteus mirabilis*, *Escherichia coli*, *Bacillus anthracis*, *Pseudomonas aeruginosa* and *Candida albicans*. The aim of the present paper was to synthesize some mixed ligand complexes derived from 1-phenylazo-2-naphthol and salicylaldehyde and to elucidate their geometrical structures, then to study their biological activities on some pathogenic bacteria

Experimental

All chemicals were reagent grade and purchased from BDH or Aldrich including CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.H₂O, Cd(CH₃COO)₂.2H₂O, salicylaldehyde, NH₄OH, C₂H₅OH, CHCl₃, DMSO and nutrient agar (OXID). The ligands under investigation have the following structures:



Measurements

The prepared mixed ligand complexes were subjected to (C, H and N) elemental analyses using 2400 CH elemental analyzer. The molar conductance measurements were carried out in DMSO using conductivity meter model CMD650 digital, were performed in chemistry department, Garyounis University, Benghazi, Libya.

The Infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/IR spectrometer (Bruker) in the range of 4000-500 cm⁻¹. The electronic absorption spectra of the complexes were measured in DMSO using UV Vis-NIR3101PC Shimadzu (Japan). The electron paramagnetic resonance spectra were recorded by using EMX ESR spectrometer (Bruker) 1998Y. All the previous chemical analyses were done at the Advanced Laboratory of Chemical Analyses, National Office for Research and Development, Tripoli, Libya.

Preparation of 1-phenylazo-2-naphthol

A (0.054 mol, 5.0 g) of aniline was dissolved in 16 mL of conc. HCl and 16 mL of water in a 250 mL 3-necked flask and cooled in ice bath. Then 20 mL of (0.058 mol, 4.0 g) sodium nitrite solution was added drop wise to the above solution with stirring and the resulting mixture was left for 1 h at 0 °C. A cooled solution (45 mL) 10% NaOH solution of 2-naphthol (0.054 mol, 7.8 g) was added drop wise to the resulting solution with stirring and the mixture was left for 1 h at 0 °C. 1-Phenylazo-2-naphthol was precipitated as red solids. The reaction mixture was filtered. The crude product was recrystallised from acetic acid and washed with ethanol. The yield of deep red crystals is about 3 g, m.p. 131 °C.

Preparation of mixed ligand complexes

The present mixed ligand complexes were prepared by mixing equal amounts (0.01 mol) of hot saturated ethanolic solutions of the first ligand (1-phenylazo-2-naphthol; 2.72 g) with the same ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ salts. The mixtures were refluxed for one hour and then the second ligand (salicylaldehyde; 1.22 g) was added in the same ratio to the previous mixtures and refluxed for three extra hours. Few drops of ammonia solution were added to adjust the pH at which the mixed ligand complexes even separated. The resulting complexes were washed several times with hot ethanol until the filtrate becomes clear, dried in air and then in vacuum over anhydrous CaCl_2 . The yield was ranged from 65-83%. The prepared mixed ligand complexes were subjected to elemental and spectroscopic analyses. The obtained complexes are insoluble in $\text{C}_2\text{H}_5\text{OH}$ but soluble in DMSO. The purity of the mixed ligand complexes were tested by TLC technique.

Antibacterial assay

The antibacterial tests were assayed according to the diffusion method. The strains of bacteria used were *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. All strains were isolated from patients in Al-Jamahiriya hospital, Benghazi, Libya. The identity of all the strains was confirmed. A bacterial suspension was prepared and added to the sterilized nutrient agar (OXID/England) medium before solidification. The medium with bacteria was poured into sterilized Petri dishes under aseptic condition. Different weights of ligands and mixed ligand complexes (0.5 mg, 1 mg and 2 mg) were placed on the surface of the culture and incubated at 37 °C for 24 h. After incubation, the average of inhibition zones was recorded (mm). Antibacterial activity was indicated by the presence of clear inhibition zones around the samples.

Results and Discussion

Microanalysis

The elemental analysis data of the mixed ligand complexes shown in Table 1 show the formation of 1: 1: 1 [M: L¹: L²] ratio. It has been found that the theoretical values are in a good agreement with the found values.

Molar conductance measurements

The molar conductance values of the synthesized mixed ligand complexes with the mentioned metal ions under investigation were determined using 10^{-3} M DMF solvent, as shown in Table 1 are in the range of 0.83 - 1.65 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. These values suggest the presence of a non-electrolyte nature⁵.

Table 1. Some physical properties of mixed ligand complexes

Chelates	M.Wt	C%	H%	N%	M.C*
$[\text{CoL}^1\text{L}^2 \cdot 2\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$	540.9	55.20(55.46)	4.02(4.81)	4.93(5.18)	1.52
$[\text{NiL}^1\text{L}^2] \cdot 2\text{H}_2\text{O}$	486.7	61.12(61.64)	4.17(4.11)	5.63(5.75)	1.33
$[\text{CuL}^1\text{L}^2] \cdot 3\text{H}_2\text{O}$	509.5	58.27(58.88)	4.53(4.32)	5.81(5.49)	0.83
$[\text{CdL}^1\text{L}^2 \cdot 2\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$	576.4	52.17(52.05)	3.98(4.16)	4.93(4.86)	1.65

*Unit of molar conductance $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, Calculated values in parentheses

Infrared spectra

The infrared spectral data of Co(II), Ni(II), Cu(II) and Cd(II) complexes shown in Table 2 reveal broad bands in the range of 3306-3400 cm^{-1} attributed to the existence of coordinated and crystallized water molecules⁶. Meanwhile, the same spectra display the bands which can be

observed in the range 1575-1620 cm^{-1} due to the $\nu_{(\text{C}=\text{O})}$ group of the salicylaldehyde ring moiety (1650 cm^{-1}) and the $\nu_{(\text{N}=\text{N})}$ group of the 1-phenylazo-2-naphthol ring moiety (1575 cm^{-1}). These bands are shifted to lower region during the complex formation indicating its participation in coordination with the mentioned metal ions. Another bands in the range of 532-698 cm^{-1} and 432 - 469 cm^{-1} which are not present in the free ligands assigned to $\nu_{(\text{M}-\text{O})}$ and $\nu_{(\text{M}-\text{N})}$ vibrations. The appearance of this vibration supports the involvement of $-\text{OH}$, $-\text{CHO}$ and $-\text{N}=\text{N}-$ group in chelation⁷.

Electronic spectra

The electronic absorption spectra of the prepared complexes were recorded in DMSO solvent as shown in Table 2. The absorption spectral data of $[\text{CoL}^1\text{L}^2.2\text{H}_2\text{O}].3\text{H}_2\text{O}$ complex show several bands shown in Table 2 attributed to the intra-ligand of the $\pi-\pi^*$ (phenyl ring), charge transfer, ${}^4\text{T}_{1\text{g}}(\text{F})\rightarrow{}^4\text{T}_{2\text{g}}(\text{F})$, ${}^4\text{T}_{1\text{g}}(\text{F})\rightarrow{}^4\text{A}_{2\text{g}}(\text{F})$ and ${}^4\text{T}_{1\text{g}}(\text{F})\rightarrow{}^4\text{T}_{1\text{g}}(\text{P})$ transitions, which propose octahedral structure⁸⁻¹⁰. The electronic absorption spectrum of $[\text{NiL}^1\text{L}^2].2\text{H}_2\text{O}$ complex reveals several bands which can be observed in the range 12903 and 14771 cm^{-1} due to the presence of $\pi-\pi^*$, $n-\pi^*$ transitions in the free ligands, charge transfer ($\text{M}\rightarrow\text{L}$) and ${}^1\text{A}_1(\text{G})\rightarrow{}^1\text{B}_1(\text{G})$ transitions. The intensity of these bands indicates square planar geometry. The electronic spectrum of the Cu(II) complex exhibits different bands Table 2 assigned due to charge transfer and ${}^2\text{B}_1(\text{G})\rightarrow{}^2\text{E}(\text{G})$ transitions. A square planar geometry was proposed¹¹. The obtained absorption bands of the $[\text{CdL}^1\text{L}^2.2\text{H}_2\text{O}].2\text{H}_2\text{O}$ complex which appeared at 13831, 22573 and 26525 cm^{-1} are attributed to a charge transfer transition. This observation supports the existence of an octahedral configuration around Cd(II) ion¹².

Electron paramagnetic resonance spectra

The electron paramagnetic resonance spectral data of $[\text{CoL}^1\text{L}^2.2\text{H}_2\text{O}].3\text{H}_2\text{O}$ and $[\text{CuL}^1\text{L}^2].3\text{H}_2\text{O}$ complexes shown in Table 2 display g_{eff} values in the range of 1.898 - 2.135. These values are deviated from the ideal free electron value. The observed deviation is attributed to the presence of a partial ionic character of the covalent bond between the Co(II) and Cu(II) ions with the mentioned ligands. Meanwhile, the obtained g_{eff} values suggest the existence of an octahedral geometry^{13,14} except Cu(II) complex which has a square planar structure¹⁵.

Table 2. Electron paramagnetic resonance spectra of the complexes, infrared assignments (cm^{-1}) and electronic spectral data (nm, cm^{-1}) of the ligands and complexes

Ligands/ Complexes	$\nu(\text{OH})$ H_2O	$\nu\text{C}=\text{O}$ (CHO)	ν (N=N)	ν (M-N)	ν (M-O)	λ_{max} nm, cm^{-1}	g_{eff}	Expected geometry
L^1	-	-	1575	-	-	-	-	-
L^2	-	1650	-	-	-	-	-	-
$[\text{CoL}^1\text{L}^2.2\text{H}_2\text{O}].3\text{H}_2\text{O}$	3400	1600	1540	432	532	324 (30864) 391 (25575) 775 (12903)	1.898	Octahedral
$[\text{NiL}^1\text{L}^2].2\text{H}_2\text{O}$	3379	1620	1538	478	698	736 (13587) 677 (14771) 723 (13831)	-	Square planar
$[\text{CuL}^1\text{L}^2].3\text{H}_2\text{O}$	3309	1620	1541	461	555	360 (27777) 287 (34843) 443 (22573)	2.135	Square planar
$[\text{CdL}^1\text{L}^2.2\text{H}_2\text{O}].2\text{H}_2\text{O}$	3400	1616	1544	469	598	377 (26525) 359 (13831)	-	Octahedral

Antibacterial activities

Table 3 shows the mean of inhibition zone of the ligands and mixed ligand complexes Co(III), Ni(II), Cu(II) and Cd(II) ions which tested at different concentrations of 0.5, 1 and 2 mg against several species of human pathogenic bacteria. The moderate effect was observed with Cu(II) complex against *Staphylococcus aureus* and *Pseudomonas aeruginosa*; which known as a resistant to most commercial antibiotic. However, no effect was observed against *Escherichia coli* with all concentrations used. Comparatively, Cd(II) complex showed significant effect against *Staphylococcus aureus* with all concentration used. In contrast no effect was observed against *Escherichia coli* and *Pseudomonas aeruginosa*. And Ni(II) did not had any effect against all bacterial tested.

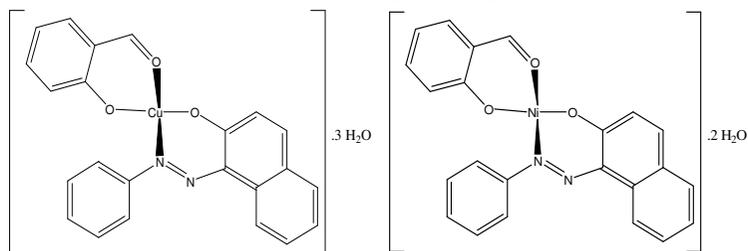
Table 3. The effect of ligands and the complexes on bacteria growth

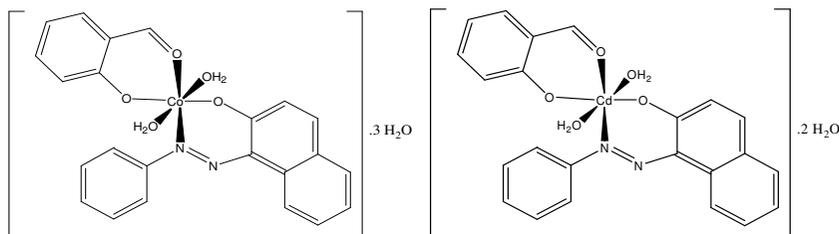
Species of bacteria Samples	Mean of inhibition zone, mm								
	<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>			<i>Pseudomonas aeruginosa</i>		
	0.5 mg	1 mg	2 mg	0.5 mg	1 mg	2 mg	0.5 mg	1 mg	2 mg
L ¹	13	21	22	12	15	21	11	13	21
L ²	13	16	19	7	9	27	7	13	16
Co(III) complex	17	21	26	13	13	13	12	15	26
Ni(II) complex	-	-	-	-	-	-	-	-	-
Cu(II) complex	-	-	-	-	-	-	14	16	26
Cd(II) complex	-	-	-	-	-	17	13	21	27

The 1-phenylazo-2-naphthol had more antibacterial activity than other ligand used. This effect may be due to the presence of –Ph, –OH and –N=N– groups which are electron-releasing. The antibacterial results evidently showed that the activity of the ligand compounds became more pronounced when coordination to the metal ions. However, Co(II) complex has the best results and presented antibacterial activity of Gram(positive) and Gram(negative) bacteria compared to other complexes and it is definitive that metal ions do play a significant role in enhancing the antibacterial activity of antibacterial agents on chelation. It is suggested that in the chelated complex, the positive charge of the metal ion is partially shared with the donor atoms and there is π -electron delocalization over the completely complex ring. This increases the lipophilic character of the metal complex and favors its permeation through lipid layers of the bacterial membranes. It is also suspected that factors such as solubility, dipole moment and cell permeability mechanisms are also influenced by presence of the metal ions¹⁶. The result showed a significant reduction of inhibition zone as the concentration of chelates decreased.

Conclusion

From the previous data [elemental analysis, molar conductance measurements infrared, electronic absorption and electron paramagnetic resonance] we can propose the following chemical formulae for the synthesized mixed ligand complexes.





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