

New Co(III) mixed ligand complexes effect on the Germination and Root length of Wheat

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Abstract

Co(III) mixed ligand complexes derived from catechol(L¹) as primary ligand with 2-aminopyridine(L²) and 2-aminobenzothiazole(L³) as secondary ligands have been prepared and characterized by conventional techniques, including; elemental analysis, electron paramagnetic resonance, infrared, electronic spectra, molar conductivity and thermogravimetric analysis. The elemental analysis data display the formation of 1:1:1 [M:L¹L²] and 1:1:1 [M:L¹:L³] complexes. The electron paramagnetic resonance spectra of the complexes reveal the oxidation of Co(II) to Co(III) which has a diamagnetic phenomena and indicate the presence of an octahedral structure. The infrared spectral data show the chelation behavior of the ligands toward Co(III) ion which is through OH, -C=N and -NH₂ groups. The electronic spectral results display the existence of $\pi \rightarrow \pi^*$ (phenyl rings), $n \rightarrow \pi^*$ (NH₂ and -C=N) and confirm the mentioned structure. The molar conductivity reveals a non-electrolytic nature. The thermogravimetric analysis data of the complexes display the existence of hydrated and coordinated water molecules. The effect of CoCl₂.6H₂O, catechol, 2-aminopyridine, 2-aminobenzathiazole and their complexes on the germination and root length of wheat seeds were evaluated at different concentrations. The prepared complexes were found to exhibit enhanced activity on germination and root length compared to ligands and metal ion.

Key Words: catechol, 2-aminopyridine and 2-aminobenzothiazole, mixed ligand complexes, Biological activity.

Introduction

Catechol, 2-aminopyridine and 2-aminobenzothiazol compounds are bidentate M.

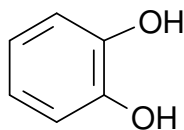
ligands and have a good ability to form many transition metal complexes.¹ Metal complexes of a ligand derived from 2,3-quinoxalinedithiol and 2,6-bis(bromomethyl)pyridine were synthesized and characterized by physical and spectroscopic measurements.² Diaz *et. al.*³ prepared Co(II) coordinate compound of ethyl-4-methyl-5-imidazolecarboxylate to study the chemical and biochemical characterization on photosynthesis and seeds.

The present work aims to prepare two mixed ligand complexes derived from catechol, 2-aminopyridine and 2-aminobenzothiazole, elucidate their geometrical structure and to study their effect on germination and root length of wheat.

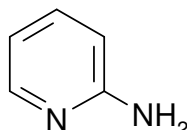
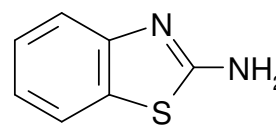
Experimental

Materials

All chemicals and reagents used in this investigation were laboratory pure (BDH or Aldrich) including $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Catechol, 2-aminopyridine, 2-aminobenzothiazole, NH_4OH , DMF, $\text{C}_2\text{H}_5\text{OH}$ and double distilled water.

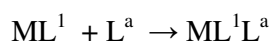
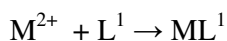


Catechol

2-aminopyridine(L^2)2-aminobenzothiazole(L^3)

Preparation of mixed ligand complexes

The present mixed complexes were prepared by mixing equal amounts (0.01 mole) of hot saturated ethanolic solution of the first ligand (catechol) with the same ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt. The mixture was refluxed for one hour, and then the second ligand (2-aminopyridine; 0.94g or 2-aminobenzothiazole; 1.50g) was added in the same ratio to the previous mixture and refluxed for three extra hours. The resulting complexes were filtered and washed several times with hot ethanol until the filtrates become clear. The solid complexes then dried in desiccator over anhydrous calcium chloride. The yield ranged from 70-85%.



$\text{M}^{2+} = \text{Co(III)}$, $\text{L}^1 = \text{catechol}$, $\text{L}^a = \text{2-aminopyridine or 2-aminobenzothiazole}$.

The dried complexes were subjected to elemental and spectroscopic analyses . The obtained complexes are insoluble in ethanol but soluble in DMF or DMSO solvent. All melting points of the complexes were measured and found to be $>360\text{ }^{\circ}\text{C}$.

Measurements

The synthesized mixed ligand complexes were subjected to (C, H, N and S) elemental analyzer. the electron paramagnetic resonance spectra were recorded by using EMX ESR spectrometer (Bruker)1998Y . The infrared spectra were obtained by using CsI disk technique on IFS-25 DPUS/IR spectrometer (Bruker) in the range of $4000\text{-}200\text{ cm}^{-1}$. The electronic absorption spectra were measured in DMF solvent using UV-Vis NIR3101PC Shimadzu (Japan). The molar conductance measurements were carried out in DMF solvent using conductivity meter model CMD650 digital, at chemistry Department, Garyounis University. The thermogravimetric analysis was achieved using Shimadzu thermal analyzer (Japan). The weight losses were measured from ambient temperature to $1000\text{ }^{\circ}\text{C}$ in rate of $10\text{ }^{\circ}\text{C}/\text{min}$. All the previous chemical analyses were done at the micro analytical center, Cairo University, Egypt .

Germination assay

Eight seeds of wheat were arranged on the filter paper (No.1) in a Petridish (9cm). The control was treated only with distilled water, then , two milliliters of each solution and the distilled water were added to the seeds on the filter paper . The experiments were carried out under natural light and at room temperature . The number of germinated seeds was counted each day for 4 days after which no further seed germination occurred . The length of the roots was measured at the end of the experiment and the elongation of the roots was determined by reference to the elongation of the control roots

Table-1: Elemental Analyses of Co(III) mixed ligand complexes

S %		N %		H %		C %		Cl	Complexes
Found	Calc	Found	Calc	Found	Calc.	Found	Calc.		
-	-	7.55	7.94	3.21	4.00	37.96	37.66	9.92 10.13	$[\text{CoL}^1\text{L}^2(\text{Cl})(\text{H}_2\text{O})].2\text{H}_2\text{O}$
8.63	8.28	7.60	7.24	2.56	2.58	40.05	40.36	9.31 9.19	$[\text{CoL}^1\text{L}^3(\text{Cl})(\text{H}_2\text{O})].\text{H}_2\text{O}$

Table-2: Infrared , UV-Vis spectra and molar conductance of Co(III) mixed ligands complexes

Δ_m	UV- Vis nm(cm^{-1})	IR(cm^{-1})					Compound ds
		$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{C=N}}$	$\delta_{\text{OH}^-\text{H}_2\text{O}}$	δ_{NH_2}	
-	-	-	-	-	-	-	L¹
-	-	-	-	1595	-	3460	L²
-	-	-	-	1605	-	3339	L³
0.17	471,432, 415, 389, 335 (21231,23148,2409 6,25707,29850)	474	667	1481	3267	-	[CoL¹L²(Cl)(H₂O)] .2H₂O
0.48	432,305 (23148,32787)	466	605	1551	3400	-	[CoL¹L³(Cl)(H₂O)] .H₂O

$$\Delta_m = \text{Molar Conductivity (Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\text{)}$$

Results and Discussion

Microanalysis

The elemental analysis data of the complexes **Table-1** show the formation of the complexes in the ratio of 1:1:1 for $[\text{CoL}^1\text{L}^2]$ and $[\text{CoL}^1\text{L}^3]$. It is found that the theoretical values are in agreement with the found values.

Electron paramagnetic resonance spectra

There is no g_{eff} values for the prepared complexes, that reveals the presence of a diamagnetic phenomena . This means that the starting metal ions $\text{Co(II)} 3d^7$ has oxidized to $\text{Co(III)} 3d^6$ and also the mixed ligand under the investigation behaves as a strong field, and an octahedral geometry was suggested for these complexes.^{4,5,6}

Infrared spectra

The Infrared band assignments of the Co(III) mixed ligand complexes, **Table-2** exhibit broad bands at 3267 and 3400 cm^{-1} , corresponding to the presence of water molecules.⁷ Meanwhile the same spectra display bands at 1481 and 1550 cm^{-1} due to –C=N group . The changes of this group compared to its original position in the free ligands at (1595 and 1605 cm^{-1}) indicating its involvement in coordination through nitrogen atom with the metal ion under investigation.⁸ The disappearance of NH_2 bands

of the free ligands indicating the participation of this group in chelation and the appearance of new bands at 446, 474 and 667 cm^{-1} assigned to the $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ vibrations.⁹ The appearance of these bands support the involvement of $-\text{C}=\text{N}$, NH_2 and OH groups via nitrogen and oxygen atoms. The same spectra exhibit two bands at 330 and 345 cm^{-1} assigned to $\nu_{\text{M-Cl}}$ vibration.¹⁰

Electronic spectra

The electronic absorption spectra of the mixed ligand complexes were recorded in DMF solvent, **Table-2**. The spectral data of the; $[\text{CoL}^1\text{L}^2(\text{Cl})(\text{H}_2\text{O})].2\text{H}_2\text{O}$ and $[\text{CoL}^1\text{L}^3(\text{Cl})(\text{H}_2\text{O})].\text{H}_2\text{O}$ complexes show several bands in the range of 305 - 471nm (32787-21231 cm^{-1}) attributed to $^1\text{A}_{1\text{g}}(\text{I}) \rightarrow ^1\text{A}_{2\text{g}}(\text{I})$, $^1\text{A}_{1\text{g}}(\text{I}) \rightarrow ^1\text{E}_{\text{g}}(\text{I})$, $^1\text{T}_{1\text{g}}(\text{I}) \rightarrow ^1\text{A}_{2\text{g}}(\text{I})$, $^1\text{A}_{1\text{g}}(\text{I}) \rightarrow ^1\text{T}_{2\text{g}}(\text{I})$, and charge transfer transitions. The octahedral structure was proposed for both complexes.¹¹

Molar conductivity

The molar conductivity of the mixed ligands complexes with the mentioned metal ion was measured using 10^{-3}M DMF solvent, **Table-2**, the obtained values suggest the presence of a non-electrolyte nature.¹²

Table-3: Thermogravimetric analysis data of the complexes

Temp °C	MO* weight loss (%)	Temp °C	No. of water molecules	Water of coordination (weight loss %)	Temp °C	No. of water molecules	Water of hydration (weight loss %)	Complexes
825	56.08 (55.20)	280-310	1	5.72 (6.20)	25-280	2	10.27 (9.60)	$[\text{CoL}^1\text{L}^2(\text{Cl})(\text{H}_2\text{O}).2\text{H}_2\text{O}]$
860	47.09 (47.20)	260-325	1	4.86 (4.22)	25-260	1	4.63 (4.50)	$[\text{CoL}^1\text{L}^3(\text{Cl})(\text{H}_2\text{O}).\text{H}_2\text{O}]$

() = Found values

MO* = metal oxide

Thermogravimetric analysis

The Thermogravimetric analysis data for Co(III) complexes, **Table-3** show a weight loss at 9.60 and 4.50% respectively, which are attributed to the presence of two and one hydrated water molecules, at temperature 280-310 and 260-325 °C respectively.

Meanwhile, these complexes have weight losses at 6.20 and 4.22% due to the existence of one coordinated water molecule at the temperature of 280-310°C and 260-323°C, respectively. The free ligands were decomposed at temperature of 310-825 °C and 325-860 °C respectively. A final product can be observed as metal oxide (Co₂O₃) at temperature, >550 °C.

Table-4: The effect of Co(II) salt, ligands and their mixed ligand complexes on the seed germination and root length

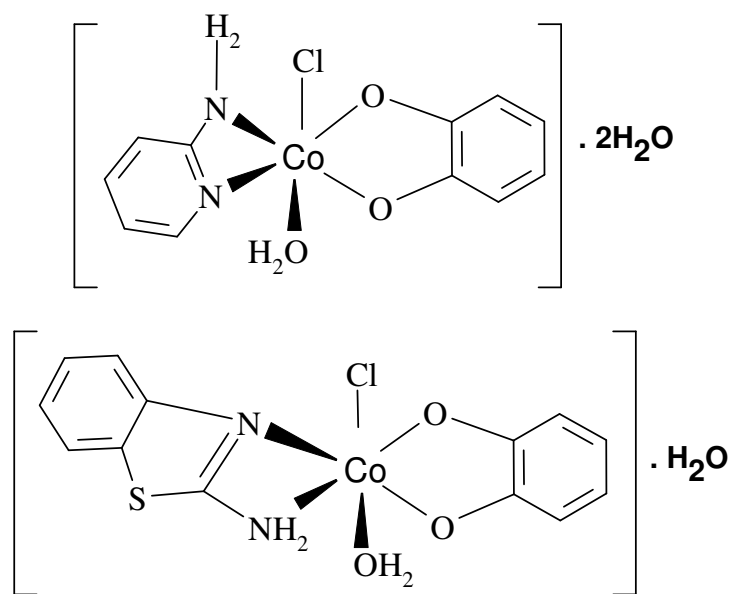
Mean of root length(mm)			Mean of germination			Compounds
0.01%	0.1%	1%	0.01%	0.1%	1%	
9.50	9.50	9.50	7.56	7.56	7.56	Control
3.83	3.00	1.10	7.56	7.43	5.52	CoCl ₂ .6H ₂ O
7.33	3.67	0.00	6.72	6.40	0.00	Catechol
3.00	1.83	0.00	7.65	6.71	1.31	2-Aminopyridine
6.50	0.00	0.00	7.40	5.24	2.93	2-Aminobenzothiazole
7.16	4.50	1.66	7.90	7.62	7.40	[CoL ¹ L ² (Cl)(H ₂ O)].2H ₂ O
8.50	2.66	1.83	7.68	7.56	7.52	[CoL ¹ L ³ (Cl)(H ₂ O)].H ₂ O

Seed germination

The method uses seed germination and root elongation in wheat plants as a parameter in the presence of varying concentrations of Co(II) salts, ligands and Co(III) complexes shown in **Table-4**, although effective concentrations of these compounds for a certain degree of inhibition were different. Wheat plant had a reduced seed germination rate and root length with increasing concentrations. The mixed ligand complex of Co(III) with 2-aminopyridine possess the highest effect on germination and root growth. The effect increases with concentration up to (0.01%), while the Co(II) salt has a moderate effect on both. On the other hand, the catechol caused a complete inhibition of germination in wheat seeds at highest concentration. No other compounds caused this kind of inhibition even at same concentration applied with some exception all compounds in the selected concentrations caused a significant decreases in germination rate of wheat plant compared to the control group seeds.

Conclusion

From the elemental analysis, electron paramagnetic resonance, infrared, electronic spectra, molar conductivity and thermogravimetric analysis, we can propose the following chemical formula for the prepared mixed ligand complexes $[\text{CoL}^1\text{L}^2(\text{Cl})(\text{H}_2\text{O})].2\text{H}_2\text{O}$ and $[\text{CoL}^1\text{L}^3(\text{Cl})(\text{H}_2\text{O})].\text{H}_2\text{O}$ as :



Figures:- The proposed chemical structures of the prepared complexes

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