



Some Co(II) Mixed Ligand Complexes Effect on the Germination and Root Length of Wheat

OMAR H. SH. AL-OBAIDI* and BAYDAA A. ATIEA

Chemistry and Biology Department, Education College for Women, Al-Anbar University, Ramadi, Iraq

*Corresponding author: E-mail: dromaralobaidi@yahoo.com

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Mixed ligand cobalt(II) complexes of the type $M(NHA)(HL)\cdot 2H_2O$ have been synthesized by using naphthalhydroxamic acid (NHA, L1) as a primary ligand and N- and/or O-donor amino acids (HL) such as L-alanine (L2) and glycine (L3) as secondary ligands. The metal complexes have been prepared and characterized by analytical and spectral methods. The elemental analysis data which display the formation of 1:1:1 [M:L1:L2] and 1:1:1 [M:L1:L3] complexes. The molar conductance studies of the complexes in DMSO at 10^{-3} concentration indicate their non-electrolytic nature for all prepared complexes. Room temperature magnetic susceptibility measurements revealed paramagnetic nature of the complexes and indicate the presence of an octahedral structure, the electronic spectral results display the existence of $\pi-\pi^*$ and $n-\pi^*$. The infrared spectral data show the chelation behaviour of the ligands toward Co(II) ion through OH, C=O and $-NH_2$ groups. A theoretical treatment of the formation of complexes in the gas phase was studied, using the HYPERCHEM-6 program for the molecular mechanics and semi-empirical calculations. The effect of $CoCl_2\cdot 6H_2O$, L1, L2, L3 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 to ligands and metal ion.

Key Words: Co(II), Mixed ligand complexes, Germination, Wheat.

INTRODUCTION

The role of mixed ligand complexes in process has been well recognized^{1,2}. The stabilities of mixed chelates are of great importance in biological systems as many metabolic and toxicological functions are dependent upon this stability. Many attempts have been made to correlate the stability of the metal-ligand complexes with their antimicrobial activity^{3,4}.

It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances⁵. Ogunniran *et al.*⁶ have proved that physical properties and antimicrobial activities are enhanced upon complexation. It has been found that a majority of the metal complexes with naphthalhydroxamic acid possess biological activity⁷. Amino acids are well known for their tendency to form complexes with metals having biological significance and metabolic enzymatic activities⁸. Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals and actinide metal ions^{9,10}. Antitumor activity of some mixed ligand complexes have also been reported^{11,12}. Therefore, it was worthwhile to study of mixed ligand complexes of Co(II), with naphthalhydroxamic acid (NHA) as a primary ligand (L1) and different amino acids (HL) such as L-alanine (L2) and glycine (L3) as a secondary ligand. The metal comp-

lexes have been characterized by metal analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electron spectra and FT-IR spectra and study their effect on generation and root length of wheat.

EXPERIMENTAL

All chemicals and reagents used in this investigation were labrotary pure (BDH chemicals, Sigma-Aldrich and E. Merk) including $CoCl_2\cdot 6H_2O$, naphthalhydroxamic acid, L-alanine, glycine, DMSO, C_2H_5OH and double distilled water.

A Fisher-100 infrared spectrophotometer was used to recorded the IR spectra as KBr and CsI disc, UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis (C.H.N) founded on (Carlo Erloa micro-analyzer type 1106), determination of all metals percentage by atomic absorption spectrophotometry on AA-680 G (Shimadzu). Electrical conductance was measured on conductivity CDC304 (Jenway4070) melting points determined by an electric heated block apparatus (Gallen Kamp) and were uncorrected. Room temperature magnetic susceptibility measurements were carried out on a B.M. 6 BRUKER type magnets, balance, diamagnetic correction was done using pascal constants.

Preparation of mixed ligand complexes: The present mixed complexes were prepared by mixing equal amounts (0.01 mol) of hot saturated ethanolic solution (20 mL) of the

TABLE-1
SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE PREPARED COMPLEXES

No.	Complexes	Colour	ΔM ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) DMSO	m.p. ($^{\circ}\text{C}$)	Yield (%)	μ_{eff} (BM)	Elemental analysis (%); Found (Calcd.)			
							C	H	N	M
1	[Co(L1)(L2)·2H ₂ O]	Pink	8	240	75	4.9	45.20 (45.15)	4.52 (4.47)	8.03 (7.99)	14.79 (14.76)
2	[Co(L1)(L3)·2H ₂ O]	Pink	7	240	80	4.4	43.61 (43.57)	4.15 (4.11)	8.30 (8.25)	15.29 (15.25)

TABLE-2
INFRARED, UV-VIS SPECTRA OF Co (II) MIXED LIGANDS COMPLEXES

No.	Complexes	UV/VIS λ_{max} (cm^{-1})	IR spectra (cm^{-1})						
			$\nu(\text{Co-N})$	$\nu(\text{Co-O})$	$\nu(\text{C=O})$	$\nu(\text{N-H})$	$\nu_{\text{OH}}(\text{H}_2\text{O})$	ν_{OH}	$\nu_{\text{assy}}(\text{COO}^-)$
1	[Co(L1)(L2)·2H ₂ O]	8810, 17805, 30105	600	480	1505	3040	3643	3340	1610
2	[Co(L1)(L3)·2H ₂ O]	8795, 17470, 30135	610	485	1500	3045	3640	3343	1590

primary ligand (NHA) (0.215 g), with the same ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt. The mixture was refluxed for 1 h and then, an aqueous solution (20 mL), of the secondary ligand (HL) (L-alanine; 0.89 g or glycine; 0.75 g) was added in the same ratio to the previous mixture with constant stirring.

The mixture was again heated in the water bath. The complexes were obtained by raising pH of the reaction mixture by adding diluted ammonia solution. The mixture was cooled and solid complex obtained was filtered, washed with water followed by ethanol. The complexes thus prepared were dried under vacuum.

Germination assay: Eight seeds of wheat were arranged on the filter paper (No. 1) in a petridish (9 cm^3). The control was treated only with distilled water, then 2 mL of each solution and distilled water were added to the seeds on the filter paper. The experiments were carried out under natural light and 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.

RESULTS AND DISCUSSION

The synthesis of mixed ligand Co (II) may be represented as follows:



where, NHA is naphthalhydroxamic acid and HL is an amino acid.

All the complexes are coloured, non-hygroscopic and thermally stable solids (Table-1) indicating a strong metal-ligand bond. The complexes are insoluble in common organic solvents such as ethanol, acetone, etc. but fairly soluble in methanol, chloroform, DMF and DMSO. The elemental analysis data (Table-1) of metal complexes is consistent with their general formulation as 1:1:1, mixed ligand complexes of the type $[\text{Co}(\text{NHA})(\text{L}) \cdot 2\text{H}_2\text{O}]$. The molar conductance value of the complexes in DMSO at 10^{-3} M concentration are very low indicating their non-electrolytic nature¹³.

The magnetic moments of the metal complexes were calculated from the measured magnetic susceptibility after employing diameter corrections. The observed μ_{eff} values presented in (Table-1) suggest the octahedral geometry for

cobalt complexes. The magnetic moments of the compounds investigated support the conclusion.

The molar conductivity of the mixed ligands complexes with the mentioned metal ion was measured using 10^{-3} M DMSO solvent (Table-1). The obtained value suggest the presence of non-electrolyte nature¹³.

The electronic absorption spectra of all the mixed ligand complexes were recorded in DMSO solvent (Table-2). The data of the $[\text{Co}(\text{L1})(\text{L2}) \cdot 2\text{H}_2\text{O}]$ and $[\text{Co}(\text{L1})(\text{L3}) \cdot 2\text{H}_2\text{O}]$ complexes show three bands observed in the region 8795-8810, 17470-17805 and 30135-30105 cm^{-1} , which may be assigned to the transitions: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{V}_1)$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{V}_2)$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})(\text{V}_3)$, respectively¹⁴ and are suggestive of the octahedral geometry around the cobalt ions¹⁵.

The FT-IR spectra of the metal complexes were obtained in KBr discs over range 4000-400 cm^{-1} (Table-2). These spectra were assessed with the infrared spectra reported for mixed ligand of amino acids and their metal complexes^{16,17} and important bands identified are:

1) A broad band present in the 3640 cm^{-1} region, which may possibly be due to asymmetric and symmetric O-H stretching vibrations. Another band present at 1605 cm^{-1} is due to H-O-H bending vibrations, representing the presence of a coordinating water molecular.

2) A presence of a strong C=O band at 1580 cm^{-1} respectively, which is coordinated through oxygen atoms acting as non-negative bidentate ligand¹⁸. In the spectra of free (NHA) ligand, C=O and C-N bands is observed near 1580 and 1420 cm^{-1} respectively, which is found to shift to lower frequency *i.e.* 1500, 1400 cm^{-1} in the spectra of complexes. A negative shift in this vibrational mode complexation specifies the coordination through oxygen donor of (NHA).

3) A band observed at 3040 cm^{-1} due to N-H symmetric vibration is at higher wave number compared with spectra of free amino acid moiety. This reveals that the amino group is coordinated through nitrogen atom. The $\nu_{\text{assy}}(\text{COO}^-)$ band of free amino acid observed at 1610-1590 cm^{-1} shifted to lower wave number in the spectra of metal complexes *i.e.* 1575 cm^{-1} . The $\nu_{\text{sy}}(\text{COO}^-)$ band of free amino acid observed at 1400 cm^{-1} is shifted to lower wave number in the spectra of metal complexes *i.e.* 1378 cm^{-1} , representing coordination of carboxylic acid group with metal ion through the oxygen atom¹⁹. The (C-N) symmetric stretching band observed at 950 cm^{-1} in the

TABLE-3
STRUCTURAL PARAMETERS, BOND LENGTH (Å) AND ANGLES (°) OF THE [Co(L1)(L2 or L3).2H₂O] COMPLEXES

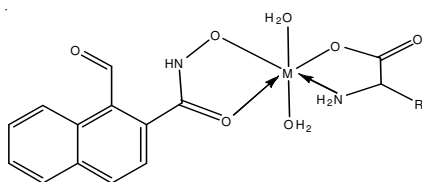
Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
C(8)-H(30)	1.1000	H(37)-O(19)-H(36)	120.0000	O(20)-Co(17)-O(16)	114.8388
C(7)-H(29)	1.1000	H(37)-O(19)-Co(17)	120.0000	N(21)-Co(17)-O(14)	107.2142
C(6)-H(28)	1.1000	H(36)-O(19)-Co(17)	120.0000	N(21)-Co(17)-O(16)	171.1656
C(4)-H(27)	1.1000	H(35)-O(18)-H(34)	120.0000	O(14)-Co(17)-O(16)	75.1996
C(3)-H(26)	1.1000	H(35)-O(18)-Co(17)	120.0000	Co(17)-O(14)-C(13)	109.5642
Co(17)-O(18)	2.2086	H(34)-O(18)-Co(17)	120.0000	H(30)-C(8)-C(9)	118.3958
Co(17)-O(19)	1.9802	H(32)-C(11)-O(12)	118.7960	H(30)-C(8)-C(7)	118.3958
O(20)-Co(17)	1.9298	H(32)-C(11)-C(1)	118.7960	C(9)-C(8)-C(7)	123.2085
N(21)-Co(17)	1.9563	O(12)-C(11)-C(1)	122.4080	H(29)-C(7)-C(8)	118.3958
O(14)-Co(17)	2.8379	H(40)-C(23)-Du(24)	24.5592	H(29)-C(7)-C(6)	118.3958
C(22)-O(25)	1.5230	H(40)-C(23)-C(22)	146.6803	C(8)-C(7)-C(6)	123.2085
C(23)-Du(24)	1.5230	H(40)-C(23)-N(21)	105.2160	N(15)-C(13)-O(14)	118.6631
C(22)-C(23)	1.0287	Du(24)-C(23)-C(22)	122.1211	N(15)-C(13)-C(2)	122.1039
N(21)-C(23)	1.5419	Du(24)-C(23)-N(21)	129.7751	O(14)-C(13)-C(2)	119.2214
O(20)-C(22)	1.5748	C(22)-C(23)-N(21)	108.1038	H(26)-C(3)-C(4)	118.3958
O(16)-Co(17)	2.9215	O(25)-C(22)-C(23)	117.8789	H(26)-C(3)-C(2)	118.3958
C(13)-N(15)	1.6287	O(25)-C(22)-O(20)	131.3688	C(4)-C(3)-C(2)	123.2085
N(15)-O(16)	1.6370	C(23)-C(22)-O(20)	110.7522	C(13)-C(2)-C(3)	125.5160
C(13)-O(14)	1.7710	H(39)-N(21)-H(38)	99.3409	C(13)-C(2)-C(1)	111.2756
C(2)-C(13)	1.4733	H(39)-N(21)-Co(17)	15.9803	C(3)-C(2)-C(1)	123.2085
C(11)-O(12)	1.3904	H(39)-N(21)-C(23)	145.3380	H(28)-C(6)-C(7)	123.2084
C(1)-C(11)	1.5230	H(38)-N(21)-Co(17)	115.3211	H(28)-C(6)-C(5)	123.2084
C(5)-C(10)	1.5230	H(38)-N(21)-C(23)	115.3211	C(7)-C(6)-C(5)	113.5831
C(1)-C(10)	1.3904	Co(17)-N(21)-C(23)	129.3578	H(27)-C(4)-C(5)	123.2085
C(9)-C(10)	1.3904	Co(17)-O(20)-C(22)	127.5631	H(27)-C(4)-C(3)	123.2085
C(8)-C(9)	1.3904	Co(17)-O(16)-N(15)	106.3923	C(5)-C(4)-C(3)	113.5831
C(7)-C(8)	1.5230	H(33)-N(15)-C(13)	115.6061	H(31)-C(9)-C(10)	123.2084
C(6)-C(7)	1.3904	H(33)-N(15)-O(16)	115.6061	H(31)-C(9)-C(8)	123.2084
C(5)-C(6)	1.3904	C(13)-N(15)-O(16)	128.7878	C(10)-C(9)-C(8)	113.5831
C(4)-C(5)	1.3904	O(18)-Co(17)-O(19)	179.8995	C(11)-C(1)-C(10)	123.2085
C(3)-C(4)	1.3904	O(18)-Co(17)-O(20)	57.0655	C(11)-C(1)-C(2)	123.2085
C(2)-C(3)	1.5230	O(18)-Co(17)-N(21)	121.2886	C(10)-C(1)-C(2)	113.5831
C(1)-C(2)	1.3904	O(18)-Co(17)-O(14)	130.4396	C(5)-C(10)-C(1)	123.2085
		O(18)-Co(17)-O(16)	58.5108	C(5)-C(10)-C(9)	123.2084
		O(19)-Co(17)-O(20)	122.8340	C(1)-C(10)-C(9)	113.5831
		O(19)-Co(17)-N(21)	58.6109	C(10)-C(5)-C(6)	123.2084
		O(19)-Co(17)-O(14)	49.6582	C(10)-C(5)-C(4)	123.2085
		O(19)-Co(17)-O(16)	121.5881	C(6)-C(5)-C(4)	113.5831

spectra of amino acids is found to be shifted to lower wave number 910 cm^{-1} in the spectra of complexes, which corroborate coordination through amine group of amino acid.

4) Some new bands of weak intensity observed in the region 600 cm^{-1} and 480 cm^{-1} may be ascribed to M-N and M-O vibrations, respectively^{20,21}, which are absent in the spectra obtained for the ligands.

5) An important feature of infrared spectra of metal complexes with NHA is the absence of the band at 3340 cm^{-1} due to the O-H stretching vibration of the OH group²². This observation specifies that the complexes are formed by deprotonation of the hydroxyl group of NHA moiety.

From the elemental analysis, electronic spectra, infrared, molar conductivity, we can propose the following chemical formula for the prepared mixed ligand complexes [Co(L1)(L2).2H₂O] and [Co(L1)(L3).2H₂O] as shown in Fig. 1 :



R=CH₃; Alanine, R=H; Glycine M= Co(II)

Fig. 1. Proposed structure of Co(II) complexes

Theoretical study: The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Fig. 2 (Table-3). As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

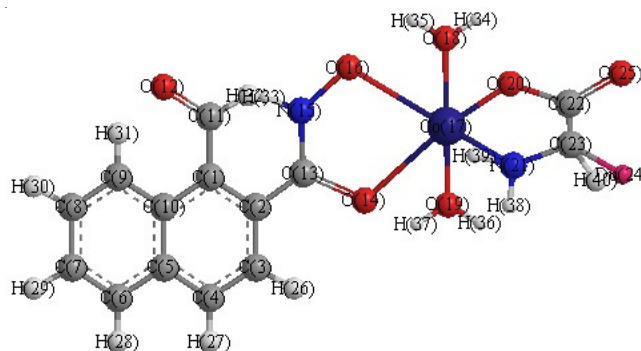


Fig. 2. Optimized structural geometry of Co(II) complexes

Seed germination: The method uses seed germination and root elongation in a wheat plants as a parameter in the presence of varying concentrations of Co(II) chloride, ligands

TABLE-4
EFFECT OF Co (II) SALT, LIGANDS AND THEIR MIXED LIGANDS COMPLEXES
ON THE SEED GERMINATION AND ROOT LENGTH

Compounds	Mean of germination			Mean of root length (mm)		
	1 %	0.1 %	0.01 %	1 %	0.1 %	0.01 %
Control	7.50	7.50	7.50	7.55	7.55	7.55
CoCl ₂ ·6H ₂ O	5.00	6.00	6.50	5.75	6.03	6.15
(L1)	4.50	5.00	6.00	5.00	5.10	5.35
(L2)	4.00	5.00	7.00	4.70	5.50	7.00
(L3)	4.00	5.50	6.00	4.80	4.85	4.95
[Co(L1)(L2)·2H ₂ O]	5.00	6.00	7.00	5.50	6.00	7.50
[Co(L1)(L3)·2H ₂ O]	4.50	6.50	7.50	4.80	6.50	7.90

and Co(II) complexes show 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 complexes of Co(II) with naphthalhydroxamic acid and alanine 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 naphthalhydroxamic acid 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 the compounds in the selected concentrations caused a significant decreases in germination rate at wheat plant compared to the control group seeds.

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