

Spectrophotometric Analysis of Cobalt (II), Nickel (II), Copper (II) and Zinc (II) Complexes with Methylenedisalicylic Acid

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ABSTRACT

Methylenedisalicylic acid was prepared as reported by the condensation reaction of salicylic acid with formaldehyde under acidic conditions. The complexes were prepared by refluxing ethanolic solutions of Methylenedisalicylic acid and some metal (II) salts. The ligand and its divalent metal complexes were characterized by solubility, melting point/decomposition temperature, molar conductance, and infrared. The ligand is white, has melting point of 238°C and percentage yield of 83%. The Co (II), Ni (II), Cu (II) and Zn (II) complexes are pink, green, brown and white, respectively. They decompose above 246°C and have percentage yield above 75%. The ligand is soluble in most common organic solvent except xylene. The metal (II) complexes are insoluble in water and most common organic solvents, but slightly soluble in methanol and DMSO. The molar conductance of the complexes in 10⁻³M solution in DMSO determined is in the range 7.8 – 8.3 ohm⁻¹cm²mol⁻¹. The metal analysis, water and ligand's compositions determined for the complexes suggested the formulae [Co₂(L-4H)(H₂O)₄].5H₂O, [Ni₂(L-4H)(H₂O)₈].7H₂O, [Cu₂(L-4H)(H₂O)₄].2H₂O and [Zn₂(L-4H)(H₂O)₈].2H₂O. The infrared spectral analysis of the free ligand showed a strong sharp band at 3440cm⁻¹ and weak band at 1213 cm⁻¹ for ν(O-H) and ν(C-O) stretching vibrations respectively. The bands in the ranges 3370 – 3400 cm⁻¹ and 600 – 678 cm⁻¹ are attributable ν(O-H) stretching frequencies for water of crystallization and coordinated water in the complexes, respectively. The bands observed in the range 453 – 481 cm⁻¹ are assigned to ν(M-O) stretching frequencies, indicating coordination of the ligand to respective metal ions. The dissociation constant of the ligand is 4.534. The ratio of metal ion to the prepared ligand is 2:1 for all the complexes.

Keywords: Methylenedisalicylic acid, formaldehyde, solubility, complex compounds, molar conductance and dissociation constant.

1. INTRODUCTION

Methylenedisalicylic acid was first prepared by Geigy (1898) who obtained it by heating a mixture of salicylic acid and formaldehyde solutions with strong hydrochloric acid (Ayman *et al.*, 2006). Many syntheses of supposedly pure methylenedisalicylic acid have been reported in the literature. However, all of them involve the treatment of salicylic acid with formaldehyde under acidic conditions yield over 93 % can be obtained using 40 % sulphuric acid (Ayman *et al.*, 2006). Gao *et al.* (1990), reported the stability constants for mixed ligand complexes of rare earth with nitrilotriacetate acids primary ligands using potentiometric titration at 25°C and ionic strength of 0.15M NaCl. The relationship between the stability constants for the mixed ligand complexes and the atomic number of rare earth has been made. It was found that the position of yttrium in the ternary system shifted to the vicinity of neodymium. In another report, Patel *et al.*, (2003), explained the physicochemical studies on square planar Cu²⁺, Ni²⁺ and Co²⁺ chelates with bis-oxime of 5, 5' – methylene(salicylaldehyde). The square planar structure

of the complexes was determined on the basis of infrared and electronic spectral measurements in conjunction with magnetic susceptibility. The thermal stability of the chelates obtained from the TG thermogram has the following order: Co (II) > Ni (II) > Cu (II). Methylenedisalicylic acid complexes of barium, magnesium and zinc were synthesized and characterized by Clemmensen and Heiman (1911), as reported by Ayman *et al.* in 2006. The analytical report established the following molecular formulae; [Ba(C₁₅H₁₀O₆)].3H₂O, [Ba₂(C₁₅H₈O₆)].8H₂O, [Mg(C₁₅H₁₀O₆)].2H₂O, and [Zn(C₁₅H₁₀O₆)].4H₂O.

Methylenedisalicylic acid can be used to effectively inhibit the attachment of ribosomes to membranes without interfering with protein synthesis (Tsuitsui *et al.*, 1978; Gianni *et al.*, 1980). The transition metal methylenedisalicylic acid complexes are applicable in areas such as electrochemistry, catalysis, bioinorganic, metallic deactivators, separation techniques and environmental chemistry (Gao *et al.*, 1990; Trevin *et al.*, 1997; Patel *et al.*, 2003).

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This paper reports synthesis and spectrophotometric analysis of cobalt (II), nickel (II), copper (II) and zinc (II) complexes with methylenedisalicylic acid.

2. EXPERIMENTAL

All chemicals and solvents used were of analytical grade (AnalaR or BDH) while salicylic acid, formaldehyde were obtained from Sigma-Aldrich and were used without further purification. Molar conductance measurements were carried out using Jenway 4010 conductivity meter. IR spectral analysis was recorded using a Fourier transformed IR Genesis series model in KBr in the range 4000 – 400 cm^{-1} . The melting point of the ligands and the decomposition temperature of their complexes were determined using Gallenkemp melting point apparatus.

Preparation of the Ligand

The ligand was prepared by adding 27.6g of salicylic acid, 9.4g of 30% formaldehyde and 180g of 50% sulphuric acid. The mixture was stirred and refluxed for 8 hours. The precipitate obtained was cooled, filtered and washed several times with cold water as well as hot water / ethanol solution to remove unreacted salicylic acid. The isolated white product was recrystallized from acetone and finally dried in air for 24 hours (Ayman *et al.*, 2006).

Preparation of the metal complexes

All the chelates were prepared by mixing ethanolic solutions of the ligand (0.005 moles) with 0.01 mole of the metal acetate. The resulting mixtures were refluxed for 1-2 hours on water bath. The coloured precipitate was filtered hot, washed thoroughly with hot ethanol and finally dried in air (Ayman *et al.*, 2006).

Determination of dissociation constant (pKa) of the ligand

To a 500 cm^3 beaker containing a magnetic stirrer was added 90 cm^3 of distilled water, 100 cm^3 of 0.2M KNO_3 and 10 cm^3 of 0.4M ligand solution. A 0.5M standardized aqueous NaOH was added to a total volume of 10 cm^3 . After each 0.5 cm^3 aliquot addition, the corresponding, pH value was recorded. The dissociation constant of the ligand was determined as reported by Gregory *et al.*, (1978).

3. RESULTS AND DISCUSSION

The prepared ligand is powdery white solid, with percentage yield 83% and melting point of 238 $^{\circ}\text{C}$. The methylenedisalicylic acid complexes of Co (II), Ni (II), Cu (II) and Zn (II) are pink, green, brown and white, have percentage yield of 94, 75, 92 and 70 65%, respectively. The complexes have decomposition temperature in the range 246 – 262 $^{\circ}\text{C}$, indicating good stability (Table 1). Solubility test carried out on the ligand its divalent metal complexes in water and some common solvents showed that the ligand is soluble in common organic solvents except xylene. The complexes are insoluble in water and common organic solvents but slightly soluble in methanol and DMSO (Table 2). The molar conductance values of metal (II) complexes determined in 10 $^{-3}$ M DMSO solution are in the range 7.8 - 8.3 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, indicating very low values (Table 3), suggesting that the complexes are non-electrolytes (Geary, 1971). The infrared spectral analysis of the free ligand showed a strong sharp band at 3440 cm^{-1} and weak band at 1213 cm^{-1} for $\nu(\text{O-H})$ and $\nu(\text{C-O})$ stretching vibrations respectively (Table 4). The spectra also indicate that methylenedisalicylic acid behaves as a tetradentate ligand, coordinating to two metal ions via the carboxyl (-COOH) and phenolic (-OH) oxygens after deprotonation of the two groups. The bands in the ranges 3370 – 3400 and 600 – 678 cm^{-1} are attributable $\nu(\text{O-H})$ stretching frequencies for water of crystallization and coordinated water in the metal (II) complexes, respectively (Byeong-Goo *et al.*, 1996; Ahmed and Akhtar, 1983; Zhang *et al.*, 2009; and Guo *et al.*, 2009). The bands observed in the range 453 – 481 cm^{-1} are assigned to $\nu(\text{M-O})$ stretching frequencies, indicating coordination of the ligand to respective metal ions. The dissociation constant of the ligand determined as reported by Gregory *et al.*, (1978) is 4.534, suggesting a weak acid (Table 5). The ratio of the metal (II) ion to the prepared ligand determined by the method of continuous variation is 2:1 for all the complexes. The empirical formulae of the complexes were determined from the known values of percent compositions of the metal ions, ligand and water of crystallization. The result supports that obtained from the method of continuous variation, and the general molecular formula of the complexes established is $[\text{M}(\text{L}-2\text{H})(\text{H}_2\text{O})_4].n\text{H}_2\text{O}$, where M is Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+} and n = 2 for Cu^{+2} and Zn^{+2} complexes; 5 and 7 for Co^{2+} and Ni^{2+} complexes respectively.

Table 1: Physical properties of the ligand and its divalent metal complexes

Compound	% Yield	Colour	M. P. (°C)	Decomposition Temp (°C)
Ligand (L)	83	White	238	-
[Co ₂ (L-4H)(H ₂ O) ₄].5H ₂ O	94	Pink	-	246
[Ni ₂ (L-4H)(H ₂ O) ₈].7H ₂ O	75	Green	-	260
[Cu ₂ (L-4H)(H ₂ O) ₄].2H ₂ O	92	Brown	-	254
[Zn ₂ (L-4H)(H ₂ O) ₈].2H ₂ O	70	White	-	262

Table 2: Solubility of the ligand and its divalent metal complexes

Compound	Propanol	Ethanol	Methanol	Acetone	DMF	DMSO	Ether	Xylene
Ligand (L)	S	S	S	S	S	S	S	S
[Co ₂ (L-4H)(H ₂ O) ₄].5H ₂ O	IS	IS	SS	IS	IS	SS	IS	IS
[Ni ₂ (L-4H)(H ₂ O) ₈].7H ₂ O	IS	IS	SS	IS	IS	SS	IS	IS
[Cu ₂ (L-4H)(H ₂ O) ₄].2H ₂ O	IS	IS	SS	IS	IS	SS	IS	IS
[Zn ₂ (L-4H)(H ₂ O) ₈].2H ₂ O	IS	IS	SS	IS	IS	SS	IS	IS

Key

S = Soluble

IS = Insoluble

SS = Slightly soluble

Table 3: Measurement of molar conductance of the complexes in 10⁻³M DMSO solution

Compound	Electrical conductivity (ohm ⁻¹ cm ⁻¹)	Molar conductivity (ohm ⁻¹ cm ² mol ⁻¹)
[Co ₂ (L-4H)(H ₂ O) ₄].5H ₂ O	8.10x10 ⁻⁶	8.10
[Ni ₂ (L-4H)(H ₂ O) ₄].7H ₂ O	8.30x10 ⁻⁶	8.30
[Cu ₂ (L-4H)(H ₂ O) ₄].2H ₂ O	7.90x10 ⁻⁶	7.90
[Zn ₂ (L-4H)(H ₂ O) ₄].2H ₂ O	7.80x10 ⁻⁶	7.80

Table 4: The infrared spectral data of the ligand and its metal (II) complexes

Compound	$\nu(\text{O-H})$ cm^{-1}	$\nu(\text{COOH})$ cm^{-1}	$\nu(\text{C-O})$ cm^{-1}	$\nu(\text{COO}^-)$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}
Ligand (L)	3440	1661	1213	-	-
$[\text{Co}_2(\text{L-4H})(\text{H}_2\text{O})_4].5\text{H}_2\text{O}$	620	-	1244	1560	481
$[\text{Ni}_2(\text{L-4H})(\text{H}_2\text{O})_4].7\text{H}_2\text{O}$	600	-	1243	1557	465
$[\text{Cu}_2(\text{L-4H})(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$	678	-	1240	1553	453
$[\text{Zn}_2(\text{L-4H})(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$	620	-	1244	1560	454

Table 5: Determination of dissociation constant of the prepared ligand

Vol. of NaOH added (cm^3)	pH	$[\text{H}^+]$	$[\text{OH}^-]$	$[\text{Na}^+]$	A_{tot}	pKa
2.0	4.32	3.28E-08	3.20E-05	4.77E-03	0.01995	1.030E-05
2.5	4.40	1.30E-09	2.66E-05	5.95E-03	0.0199	1.16E-05
3.0	4.45	1.06E-10	2.37E-05	7.12E-03	0.0199	1.35E-05
3.5	4.48	5.70E-11	2.22E-05	8.29E-03	0.0198	1.62E-05
4.0	4.52	5.19E-11	2.02E-05	9.45E-03	0.0198	1.89E-05
4.5	4.55	3.59E-11	1.89E-05	1.06E-02	0.0197	2.24E-05
5.0	4.59	2.99E-11	1.72E-05	1.18E-02	0.0197	2.62E-05
5.5	4.64	2.85E-11	1.53E-05	1.29E-02	0.0196	3.02E-05
6.0	4.70	2.49E-11	1.34E-05	1.40E-02	0.0196	3.50E-05
6.5	4.74	2.27E-11	1.22E-05	1.52E-02	0.0195	4.42E-05
7.0	4.79	2.07E-11	1.09E-05	1.63E-02	0.0195	5.87E-05
7.5	4.89	2.07E-11	8.62E-06	1.74E-02	0.0194	8.14E-05
8.0	5.01	2.07E-11	6.56E-06	1.85E-02	0.0194	1.77E-04

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