

SYNTHESIS, CHARACTERIZATION & ANTIMICROBIAL STUDIES OF BIMETALLIC COMPLEXES OF Ni(II) & Cu(II)-THIOL WITH Rb & Cs METAL SALTS OF SOME ORGANIC ACIDS

BIRENDRA KUMAR

P.G. Deptt. of Chemistry, Maharaja College (VKSU), Ara - 802301 (Bihar), India

POONAM

Research Scholar, VKSU, Ara - 802301

AND

ASHA KUMARI

Deptt. of Chemistry, Patna Science College (PU) Patna - 800005 (Bihar), India

RECEIVED : 8 December, 2018

Some noble bimetallic complexes of the general formula $[M_a(THL)_2.M_bL]$; where $M_a = Ni(II)$ or $Cu(II)$, $M_b = Rb$ or Cs , $THL = 3$ -hydroxy-2-methyl-1,4-naphthaquinone (Thiocol), $L =$ deprotonated *o*-nitrophenol or 2,4-dinitrophenol have synthesized. The complexes have been characterized by elemental analysis, infrared, electronic absorption spectra, molar conductance and magnetic moment measurements. IR spectral studies show coordination of Rb or Cs metal through oxygen atoms of O-H(phenolic) groups of metal chelate, $[M_a(THL)_2]$. The electronic spectral and magnetic moment data indicate their octahedral geometry. The antimicrobial results showed that the activity of the ligand/complex ligands became more pronounced when coordinated to the metal ions.

INTRODUCTION

3-Hydroxy-2-methyl-1, 4-naphthaquinone (Thiocol) found in many plant systems [1], and has important analytical applications. It provides a potential binding sites for the metal ions. It has been well investigated for its coordination behavior towards the transition metals as well as non-transition metals [2-8]. In this communication, we have taken Ni(II) & Cu(II)-thiocol, $[M_a(THL)_2]$ as complex ligands and synthesized some noble bimetallic complexes with Rb & Cs metal salts of some organic acids (*o*-nitrophenol & 2, 4-dinitrophenol).

EXPERIMENTAL

O-nitrophenol, 2, 4-dinitrophenol, thiocol, nickel(II) acetate and copper(II) chloride of AR grade were used as such.

Preparation of Ni(II) & Cu(II) metal chelates of thiocol, $[M_a(THL)_2]$: 0.01 mole of thiocol was dissolved in 100 mL distilled water. 0.01 mole nickel(II) acetate/copper(II) chloride was dissolved in 50 mL warm distilled water. The two solutions were mixed and

mixture was refluxed on magnetic hot plate at 70 - 80°C for nearly 1-2 hours with continuous stirring. The colour of solution changed to red/red-brown, and on cooling purple/yellowish brown precipitate of Ni(II)/Cu(II) thiocol chelate was separated out. It was filtered, washed with distilled water and then dried in an electric oven at 100°C.

Preparation of Rb & Cs metal salts of some organic acids, M_bL : 95% Ethanolic solution of 0.02 mol of organic acid(o-nitrophenol or 2,4-dinitrophenol) and 0.01 mol of RbOH/CsOH were mixed. The whole mixture was heated on water bath for about 30 minutes when clear solution was obtained. It was filtered, concentrated and cooled to get characteristic colour precipitate. The precipitate was filtered, washed with absolute ethanol and finally dried in an electric oven at 80°C.

Preparation of Bimetallic complexes, $[M_a(THL)_2 \cdot M_bL]$: 0.001 mole of Ni(II) or Cu(II)-thiocol, $[M_a(THL)_2]$ was taken in absolute ethanol and 0.001 mole of Rb or Cs metal salt of organic acid (o-nitrophenol or 2,4-dinitrophenol) was added to it. On stirring, colour of the mixture solution changed. The whole mixture was refluxed on magnetic hot plate at 70-80°C for 1-2 hours with continuous stirring, A characteristic colour precipitate of the complex was separated out. It was filtered, washed thoroughly with absolute ethanol and dried in an electric oven at 100°C.

Table 1. Colour, decomp. temp., molar conductance, magnetic moments & elemental analysis of the compounds

Compound	Colour	M.Pt./Deco. Temp. (°C)	Molar cond. ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Magnetic moment (in BM)	% Analysis Found/(Calc.)				
					C	H	N	M_a	M_b
[Ni(THL) ₂]	Purple	275d	2.6	1.70	50.22 (50.37)	2.94 (3.00)	8.20 (8.39)	18.84 (19.04)	– –
[Ni(THL) ₂ .RbONP]	Reddish brown	>300	6.4	1.80	51.03 (51.20)	2.64 (2.74)	2.05 (2.13)	8.82 (8.94)	12.84 (13.03)
[Ni(THL) ₂ .RbDNP]	Yellowish brown	>300	5.8	2.15	47.84 (47.92)	2.34 (2.42)	3.81 (3.99)	8.23 (8.37)	12.02 (12.19)
[Ni(THL) ₂ .CsONP]	Reddish brown	>300	7.0	1.85	47.63 (47.75)	2.48 (2.56)	1.81 (1.99)	8.23 (8.34)	18.70 (18.89)
[Ni(THL) ₂ .CsDNP]	Pale brown	295d	8.5	1.95	44.69 (44.88)	2.18 (2.27)	3.57 (3.74)	7.72 (7.84)	17.68 (17.75)
[Cu(THL) ₂]	Yellowish brown	190md	2.9	–	51.01 (51.11)	2.91 (3.04)	8.35 (8.52)	17.62 (17.66)	– –
[Cu(THL) ₂ .RbONP]	Deep brown	289d	9.0	–	50.77 (50.83)	2.61 (2.72)	2.05 (2.12)	9.42 (9.61)	12.78 (12.93)
[Cu(THL) ₂ .RbDNP]	Reddish brown	>300	7.8	–	47.43 (47.59)	2.35 (2.41)	3.81 (3.96)	8.83 (8.99)	12.01 (12.11)
[Cu(THL) ₂ .CsONP]	Brown Deep	270d	10.0	–	47.34 (47.43)	2.48 (2.54)	1.81 (1.97)	8.82 (8.96)	18.60 (18.76)
[Cu(THL) ₂ .CsDNP]	brown	285d	7.5	–	44.48 (44.60)	2.20 (2.25)	3.66 (3.72)	8.38 (8.43)	17.42 (17.64)

RESULTS & DISCUSSION

Some physical properties of the metal chelates and bimetallic complexes are given in Table-1. All the complexes are characteristic colours and are different from the metal chelates. The melting/decomposition temperatures of the complexes are considerably higher than respective metal chelates, indicating their higher stabilities. They are generally slightly soluble in methanol, ethanol, DMF but insoluble in benzene, chloroform etc.

Molar conductance : Molar conductance values of the compounds were measured in methanol at 30°C at a concentration of 10^{-3} M. The low values (3.8 - 10.1 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) of molar conductances of the metal chelates/complexes, indicate that they are non-electrolyte/covalent in nature [9].

Infrared spectra : Infrared spectra of metal chelates and their bimetallic complexes were recorded in KBr phase between 4000 - 400 cm^{-1} with the help of Perkin Elmer IR spectrophotometer. Pertinent IR data for these compounds are shown in Table - 2.

Table 2. Infrared and electronic absorption spectral data of the metal chelates & bimetallic complexes

Compound	IR absorption bands (in cm^{-1})					Diffuse reflectance (in nm)
	$\nu_{\text{O-H}}$	$\nu_{\text{C=O(free)}}$	$\nu_{\text{C=O(bonded)}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$	
[Cu(THL) ₂]	3367	1648	1603	1277	510, 480	352
[Cu(THL) ₂ .RbONP]	3413	1645	1523	1219	505	322, 351, 391, 402, 416
[Cu(THL) ₂ .CsONP]	3420	1643	1549	1219	515, 468	315, 322, 351, 391, 429
[Cu(THL) ₂ .CsDNP]	3452	1649	1519	1218	505, 460	312, 351, 391, 409
[Ni(THL) ₂]	3399	1650	1600	1292	553, 445	351, 362, 423, 448, 490
[Ni(THL) ₂ .RbONP]	3451	1660	1567	1217	513	351, 366, 387, 423, 430
[Ni(THL) ₂ .RbDNP]	3440	1648	1518	1217	522, 480, 450	365, 391, 398, 416, 427
[Ni(THL) ₂ .CsDNP]	3422	1627	1529	1218	508, 465	315, 337, 391

The moderately strong band present in thiocol at 3347 cm^{-1} is attributed to the stretching -OH vibration frequency. The free carbonyl and the hydrogen bonded carbonyl are assigned to 1670 cm^{-1} and 1630 cm^{-1} respectively. In the infrared spectra of metal chelates, [Ni(THL)₂] and [Cu(THL)₂], -OH stretching frequency of ligand (thiocol) is missing because of hydrogen atom of -OH group is replaced by Ni/Cu metal. From infrared spectra, it is observed that the C=O frequency of [Ni(THL)₂] at 1600 cm^{-1} shifted down in the region 1518 - 1567 cm^{-1} in its bimetallic complexes and corresponding C=O frequency of [Cu(THL)₂] at 1603 cm^{-1} , again shifted down in the region 1519 - 1598 cm^{-1} in its bimetallic complexes. The characteristic absorption band of C-O(phenolic) stretching frequency observed at 1292 cm^{-1} and 1277 cm^{-1} in the metal chelates again shifted down in the region 1217 - 1219 cm^{-1} in the bimetallic complexes, which indicate increased bond order between the C & O atoms as a result of coordination of oxygen atom to Rb/Cs metal. Further in the low frequency region, the band observed in the region 445 - 553 cm^{-1} may be assigned to M-O band frequency [10]. This suggests bonding between the metal chelates and Rb/Cs metal generally appear by dative bonding via oxygen atom of C-O(phenolic).

Electronic spectra : Electronic spectra of the metal chelates and their bimetallic complexes were recorded on Systronic double beam UV-VIS spectrophotometer - 2202 in methanol. The bands observed in electronic spectra of the metal chelates and their bimetallic complexes are given in Table - 2.

The electronic spectra of $[\text{Ni}(\text{THL})_2]$ and its bimetallic complexes display bands in the region 315 - 398 nm due to charge transfer. In $[\text{Ni}(\text{THL})_2]$, bands in the region 423 - 490 nm due to d-d transitions, and suggest the square planar of Ni(II) complexes with C.No. 4. The electronic spectra of its bimetallic complexes also gave similar type of bands in the region of 416 - 430 nm. This indicates that there is no change in stereochemistry of the complexes. This is also supported by the magnetic moment data.

In electronic spectra of $[\text{Cu}(\text{THL})_2]$ and its bimetallic complexes, bands appear in the region 312 - 391 nm due to charge transfer. The electronic absorption bands of metal chelates and its complexes in the region 402 - 429 nm assigned to d-d transition, and suggest their square planar geometry.

Magnetic moment : Magnetic moment of the metal chelates and bimetallic complexes have been measured by Can Faraday magnetic susceptibility balance at 30°C. The magnetic moment values are shown in Table - 1. The magnetic moment of $[\text{Cu}(\text{THL})_2]$ has been found to be 1.71 BM, suggesting its square planar geometry(C.No. 4). The magnetic moment values of the complexes found in the range 1.78 - 2.19 BM, which corresponds to the presence of one unpaired electron. This indicates that stereochemistry of the metal chelate remain almost same in the complexes. Very low values(nearly zero) of magnetic moments of $[\text{Ni}(\text{THL})_2]$ and its bimetallic complexes, suggesting their diamagnetic nature, and also their square planar geometry(C.No. 4).

STRUCTURE & BONDING

On the basis of elemental analysis, general (molecular) formula of the bimetallic complexes has been suggested as $[\text{M}_a(\text{THL})_2.\text{M}_b\text{L}]$. The infrared, electronic spectral and magnetic moment studies suggested following probable structure for the complexes (Fig.1) :

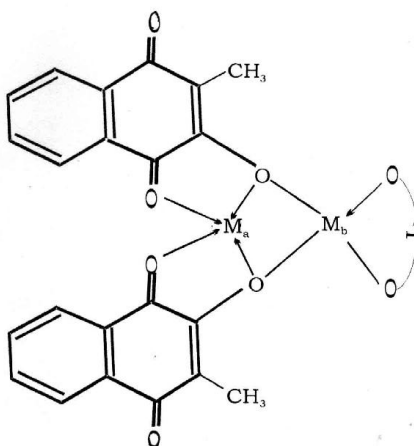


Fig. 1

where $\text{M}_a = \text{Ni}(\text{II})$ or $\text{Cu}(\text{II})$, $\text{M}_b = \text{Rb}$ or Cs & $\text{L} = \text{o-nitrophenol}$ or $2,4\text{-dinitrophenol}$

Microbial studies : Zone of inhibition of the synthesized compounds against a number of gram positive and gram negative pathogens bacteria and fungus were recorded in suitable medium at a concentration of 0.5 $\mu\text{g}/\text{mL}$ and 1 $\mu\text{g}/\text{mL}$ at 30°C for 24 hours for bacteria and at 26°C for 48 hours for fungi using Serial Dilution Method [11]. The inhibition zone of the

compounds were recorded in Table - 3. The antimicrobial results evidently show that the activity of the ligand/complex ligands became more pronounced when coordinated to the metal ions. It is however, not possible to make out exactly which metal ion is playing more antimicrobial role against one or other bacterial species but, it is definitive that metal ions do play a significant role in enhancing the antimicrobial activity of the ligand on chelation.

Table 3. Antimicrobial activity of some of the metal chelates & bimetallic complexes

Organism	[Cu(THL) ₂]	[Ni(THL) ₂]	Inhibition zone(mm) of the compound					
			[Cu(THL) ₂ , RbONP]	[Cu(THL) ₂ , RbDNP]	[Cu(THL) ₂ , CsONP]	[Ni(THL) ₂ , RbONP]	[Ni(THL) ₂ , CsONP]	[Ni(THL) ₂ , CsONP]
<i>E. coli</i>	++	+	++	+++	++	++	++	++
<i>S. aureus</i>	+	+	+++	++	+++	++	+++	++
<i>C. albicans</i>	+	+	++	++	++	++	+	+
<i>A. flavus</i>	-	-	+	+	+	-	-	-
<i>P. aeruginosa</i>	-	-	+	-	+	-	-	-

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