

Metal Complexes of N-BIS (2-Hydroxyethyl) Glycine (Bicine)

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ABSTRACT

The medical importance of chelating agents hinges on the fact that metals play many critical roles in the life of living organisms. In the human body, metabolism depends not only on sodium, potassium, magnesium and calcium but also to a considerable degree on trace amounts of iron, cobalt, copper, zinc, manganese and molybdenum. On the other hand, certain other metals like mercury, lead and cadmium, even in trace amounts, are highly toxic to the body. The dependence of living organisms on metals is well exemplified by the observation that one third of all enzymes have a metal ion as an essential component.^[1] Also it has been reported that all most all globular proteins bind a wide range of metal ions.^[2]

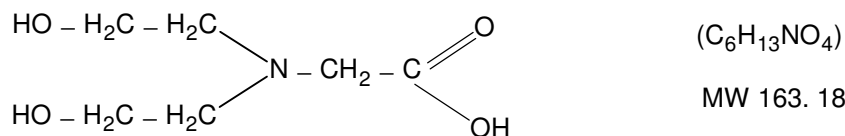
It is proposed to study the metal binding characteristics of some selected pharmaceuticals mentioned below

N-Bis(2-hydroxyethyl)glycine, commonly known as bicine, is potential chelating compound containing hydroxyl oxygen, carboxyl oxygen and tertiary nitrogen as key atoms.

Keywords: Bicine,

6. INTRODUCTION

Bicine, a derivative of glycine, exists as a white solid and forms colourless aqueous solution containing the dipolar ion $(\text{HOH}_4\text{C}_2)_2\text{NH}-\text{CH}_2-\text{COO}^-$. It can be purified by dissolving in a small amount of hot water and precipitating with ethanol. Bicine contains a nitrogen atom, as well as one or more oxygen atoms (alcoholic or carboxylic) in suitable positions to form five membered chelate rings.



Copper(II) complex of bicine (blue coloured crystals) was reported and found useful as copper donor in the developing of phthalocyanine dyes on fibers^[3]

Experimental procedure

Conductivity Measurement^[4]

Conductivity measurements for the metal complexes were carried out on a Metrohm 660 conductometer using a dip type cell incorporated with a temperature sensor.

Infrared Spectral Analysis^[5,6]

Infrared spectra of the compounds were taken either as potassium bromide pellets or as nujol mull on a SP 1200 infrared spectrophotometer in the range 4000–400 cm^{-1}

Magnetic Susceptibility Measurement^[7,8,9]

Magnetic susceptibilities for the metal complexes were measured on a Cahn 2000 magnetic balance.

Material used

N-bis(2-hydroxy ethyl glycine) (Fluka AG, Switzerland)

Common organic solvent

Distilled water, Ethyl Alcohol, Sodium hydroxide

Preparation of Metal Complexes of N-Bis(2-hydroxyethyl)-glycine (Bicine)

To prepare metal complexes of bicine other than the cobalt complex, an aqueous solution of bicine (20 mmol) was mixed with an aqueous or alcoholic solution of metal salt (10 mmol). The solution was boiled and concentrated over a water bath to a volume of ten to fifteen ml. The concentrate was allowed to stand at room temperature to get crystals of the metal complex. In some cases the solution was kept in a refrigerator to obtain the complex.

In the case of cobalt, the pH of the aqueous solution containing the metal salt and bicine in 1:2 ratio was raised using dilute sodium hydroxide solution. The precipitate formed was filtered, washed with distilled water and then dried in a vacuum desiccator.

7. RESULTS AND DISCUSSION

The physical and analytical data of bicine and its metal complexes are presented in Table 1. The results of elemental analysis for the metal, carbon, hydrogen, and nitrogen were found to be in agreement with the proposed molecular formula of the metal complex.

Table 1: Physical and Analytical Data of Bicine and Its Metal Complexes

S.No.	Compound#	Colour	M.P. (°C)*	Elemental Analysis							
				Calculated (%)				Found (%)			
				M	C	H	N	M	C	H	N
1.	Bicine (C ₆ H ₁₃ NO ₄)	White	190	–	44.16	8.03	8.58	–	44.36	8.27	8.51
2.	Mg(BC)	White	157	13.10	38.86	5.98	7.55	12.89	38.47	5.77	7.58
3.	[Mn(BCH)Cl ₂] ₂ H ₂ O	Light pink	120	16.90	22.17	5.23	4.31	16.76	22.10	5.67	4.40
4.	Co(BC) ₂	Pink	325d	15.30	37.41	6.28	7.27	15.42	37.30	6.74	7.06
5.	Cu(BCH)Cl ₂	Green	160	10.67	24.21	4.40	4.71	10.92	24.99	4.69	4.81
6.	Zn(BC)Cl	Cream	125	24.86	27.40	4.96	5.30	24.54	27.90	5.13	5.29
7.	Cd(BC)Cl	White	118	36.26	23.24	4.22	4.52	35.92	23.08	4.66	4.39

BCH = bicine; BC = deprotonated bicine

* d = decomposing

8. CONDUCTIVITY

The conductivity was measured on millimolar solutions of bicine and its metal complexes in dimethylformamide. The molar conductivity values calculated for these compounds are given in Table 2. Bicine complexes of zinc(II) and cadmium(II) were found to have higher values of molar conductivity than expected for 1:2 electrolytes. This could possibly be due to solvolysis of these compounds (dimethylformamide itself has ability to coordinate the metal ions). Magnesium(II), cobalt(II) and copper(II) complexes have lower conductivity than expected for electrolytes in dimethylformamide (60 ohm⁻¹.cm².mol⁻¹) at room temperature. The manganese(II) complex of bicine, however, was found to be conductive and the value of molar conductivity (135 ohm⁻¹.cm².mol⁻¹) falls in the range expected for 1:2 electrolytes.^[10]

9. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibilities of manganese(II), cobalt(II) and copper(II) complexes of bicine were measured at room temperature. The values of effective magnetic moment in Bohr Magnetons are given in Table 2.

The room temperature magnetic moment calculated for manganese(II) complex of bicine is 4.73 (BM). This lower magnetic moment, μ_{eff} when compared to the expected moment of about 5.92 BM for divalent manganese ions might be due to electron spin interaction between two closer manganese(II) ions in an octahedral environment created by the bridging carboxylate group of bicine

10. INFRARED SPECTRAL STUDY^[11]

Infrared spectra of bicine and its metal complexes were recorded as potassium bromide pellets in the region 4000–400 cm^{-1} and as polyethylene film in the region 700–30 cm^{-1} . The changes in the energy of absorptions by bicine on coordination to the metal ions were not so clear that one could not assign the various vibrational frequencies unambiguously. This might be due to intra- and inter- molecular hydrogen bonding interactions in bicine to a large extent which are reflected in the vibrational frequencies^[12,13] corresponding to hydroxyl and carbonyl groups.

A strong, broad absorption (3550–3000 cm^{-1}) which centered around 3200 cm^{-1} in the spectrum of bicine (Fig. 5.3) might be due to O–H stretching vibration. Infrared spectra of the metal complexes showed an overall shift towards lower energy with respect to this O–H stretching frequency and exhibited many superimposed peaks³⁾ in the ranges 3380–3420 cm^{-1} , 3230–3280 cm^{-1} , and 3030–3080 cm^{-1} (see Table 3). This indicates the destruction of hydrogen bonding in the molecule of bicine to a considerable extent on metal-binding. The vibrational absorptions due to water molecules in the metal–bicine complexes further complicated the infrared spectra of the complexes. Infrared bands in the region 3020–3080 cm^{-1} might be due to metal–bound O–H group stretching.

Table 2: Magnetic Susceptibility and Conductivity Data of Bicine and its Metal Complexes

S.No.	Compound	Magnetic Moment, μ in BM	Molar Conductivity, Λ_M in DMF ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)
1.	Bicine($\text{C}_6\text{H}_{13}\text{NO}_4$)	–	2.75
2.	Mg(BC)	diamagnetic	7.10
3.	[Mn(BCH)Cl ₂] ₂ H ₂ O	4.73	135.00
4.	Co(BC) ₂	4.63	4.40
5.	Cu(BCH)Cl ₂	1.93	47.00
6.	Zn(BC)Cl	diamagnetic	–*213
7.	Cd(BC)Cl	diamagnetic	–*216

* *High values of molar conductivity possibly due to solvolysis*

11. THERMAL DECOMPOSITION STUDY^[14]

Bicine and its metal complexes were heated at a rate of 10°C per minute upto 800°C in static air. Bicine itself decomposed completely with one endothermic peak at 250°C and one small but broad exothermic peak around 510°C. The crucible was found to be empty at 610°C. Due to swelling of the samples around 330°C, thermal analyses in the case of manganese(II), zinc(II) and cadmium(II) complexes of bicine were abandoned.

Table3: Infrared Spectral Data of Bicine and its Metal Complexes*

Assignment	Bicine	Mg-BC	Mn-BC	Co-BC	Cu-BC	Zn-BC	Cd-BC
ν_{O-H}	3200vb,s – –	3250vb,s 2900s –	3400vb,s 3180s 3080s	3270vb,s 3020s –	3230vb,s 3060s –	3380vb,s 3080s –	3380vb,s 3060s –
$\nu_{C=O}$	1650s – – – –	1660s 1640s 1625s 1610s –	– 1640s 1625s 1610s –	1740s 1720s 1650s 1590s –	1760s 1750s – 1590s 1560s	1670s 1640s 1610s 1590s –	1650s 1625s 1610s – –
$\nu_{C=O} + \nu_{C-N}$	1400s –	1410s –	1410s –1	1425s 1395s	1410s –	1420s –	1410s –
Aliphatic ν_{C-N} + ν_{C-COO}	1235s 1200s	1220s –	1215s –	1235s 1210s	1235s –	1220s	1220s –
O-H deformation	1100s 1090m	1095s 1075m	1090s 1070m	1065s 1070m	1050s 1075m	1085s 1070m	1090s 1070m
$\nu_{C-O} + \nu_{C-C-N}$	1040s	1060s	1050s	1040s	1060s	1050s	1050s
δ_{O-H} out of plane (alkanolamine)	695m	610m	610m	700m	620m	615m	610m
ν_{M-O}	– –	– 485	505 485	530 520	510 480	485 –	480 –
ν_{M-N}	–	440	430	440	420	440	430
$\nu_{M-O} + \nu_{M-N}$	–	410	410	–	–	410	410

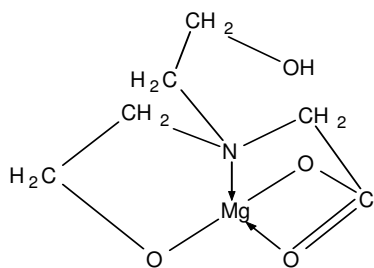
* *Spectra recorded in KBr; vibrational frequencies in cm^{-1} .*

δ = strong; m = medium; weak and vb = very broad

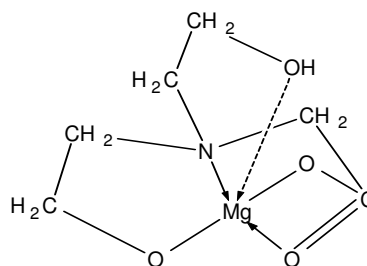
12. CONCLUSION

Bicine can act as a multidentate ligand binding the metal ion through two carboxylic oxygen, two alcoholic (hydroxyethyl) oxygen and one imine nitrogen atoms. The ligational behaviour of bicine may vary depending on the nature of metal salts and solvent used and other experimental conditions like pH of the solution, etc. Based on various spectral, magnetic and thermal studies on the metal–bicine complexes prepared, the following suggestions are made regarding the structural aspects.

Magnesium(II) complex of bicine (non–conductive in dimethylformamide) may contain deprotonated ligand binding the metal ion through nitrogen, two carboxylic oxygen and one or both alcoholic oxygen atoms. The mode of chelation with respect to carboxyl group may be bidentate or bridging type (not so clear from infrared spectral data). Hence the structure of the magnesium(II) complex may be either tetrahedral or five coordinate as shown below.

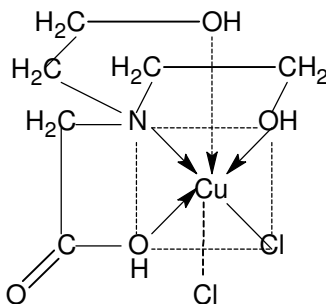


(Tetrahedral)



(Five coordinate)

The green coloured copper(II) complex of bicine, $[\text{Cu}(\text{BCH})\text{Cl}_2]$ may have tetragonally distorted octahedral structure in which bicine probably acts as a tetradentate ligand. The presence of higher energy vibrational bands (1760 and 1750 cm^{-1}) in the infrared spectrum of the complex indicated the non–involvement of carbonyl group in metal binding. In that case, the ligand may bind the metal ion through nitrogen, carboxylic oxygen and two alcoholic oxygen atoms as shown below.



The above conclusions, however, remain subjective to further structure investigation like single crystal polarized electronic spectral study, X-ray crystallographic study, etc.

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