

## Synthesis and Characterization of Mixed Ligand Copper(II) Complexes of Hippuric Acid and Nitrilotriacetic Acid

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Mixed ligand copper(II) complexes,  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}] \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}]$  formed with hippuric acid and nitrilotriacetic acid have been synthesized and characterized by their elemental analysis, spectral (IR, electronic and  $^1\text{H}$  NMR spectra) and magneto-chemical studies. Hippuric acid acts as a bidentate ligand and the coordination occurs through carboxylate oxygen and the nitrogen of the amido group. Nitrilotriacetic acid shows tetradentate behaviour by coordination through three carboxylate oxygen atoms and the nitrogen atom. The complexes have been suggested to show octahedral structures.

**Key Words:** Synthesis, Octahedral copper(II) complexes, Hippuric acid, Nitrilotriacetic acid.

### INTRODUCTION

Mixed ligand complexes are known to play a vital role in biological systems<sup>1</sup> and continued to attract interest in recent years. The formation of some mixed ligand transition metal complexes in solution, with aspartic acid or glutamic acid as a primary ligand and nucleic acid bases, uracil and thymine as secondary ligands, have been potentiometrically studied<sup>2</sup>. Some mixed ligand transition metal complexes formed with glycine, nitrilotriacetic acid or histidine as primary ligand and adenine, guanine, uracil, thymine or hippuric acid as secondary ligand have also been studied<sup>3–5</sup>. This paper describes the synthesis and characterization of new mixed ligand copper(II) complexes formed with hippuric acid and nitrilotriacetic acid.

### EXPERIMENTAL

Solutions of hippuric acid (Fluka) and nitrilotriacetic acid (Fluka) were prepared by dissolving them in an equivalent of sodium hydroxide. The solution of copper(II) sulphate (BDH) was prepared in an equivalent of hydrochloric acid to suppress its hydrolysis. To prepare the metal complex, the two ligands were mixed with 0.1 M metal-ion solution in a 1 : 1 : 1 molar ratio at room temperature. At first, nitrilotriacetic acid was mixed with copper(II) sulphate solution followed

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by hippuric acid and the pH of the solution was adjusted to *ca.* 5.0 by adding sodium hydroxide. On adding nitrilotriacetic acid to the metal ion solution, a blue-coloured solution was obtained at pH 3.0, which was raised to 4.10 by adding sodium hydroxide. On the addition of hippuric acid solution to this solution, the pH of the resulting blue solution was adjusted to *ca.* 5.0 by adding sodium hydroxide solution. The clear blue solution was then concentrated over a steam bath and allowed to crystallize. The blue crystal product was then filtered and washed first with distilled water and then with ethyl alcohol and dried in a vacuum desiccator. On heating the complex in an air oven it loses water and the green anhydrous crystalline complex is formed.

The IR spectra of the ligands and metal complexes were recorded on a Perkin-Elmer FTIR 2000 spectrophotometer in the range 4000–400  $\text{cm}^{-1}$  in KBr discs. The magnetic susceptibilities of the complexes were measured at room temperature using Johnson Matthey Alfa product magnetic susceptibility balance. Shimadzu UV-Vis-2501 PC spectrophotometer model TCC-240 A was used to record the electronic spectra in methyl alcohol in 200–1000 nm range. The  $^1\text{H}$  NMR spectra of ligands and the complexes were taken on a Bruker 300 ultrashield 300 MHz machine. The elemental analysis (C, H, N) was carried out on a Varioel CHN O/S elemental analyzer.

## RESULTS AND DISCUSSION

### Elemental analysis

1. Disodium(hippurato)(nitrilotriacetato)copper(II) tetrahydrate: Blue crystals. Anal. (%) Calcd. for  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}].4\text{H}_2\text{O}$ : Cu 11.60, C 32.88, H 4.06, N 5.11; Found: Cu 11.94, C 32.65, H 4.36, N 5.43.
2. Disodium(hippurato)(nitrilotriacetato)copper(II): Green crystals. Anal. (%) Calcd. for  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}]$ : Cu 13.35, C 37.86, H 2.97, N 5.88; Found: Cu 13.67, C 38.26, H 3.32, N 6.01.

### IR Studies

Nitrilotriacetic acid and hippuric acid show the characteristic  $\nu(\text{C}=\text{O})$  absorption band for the COOH group at 1731 and 1746  $\text{cm}^{-1}$  respectively, which vanishes in case of metal complexes. Instead, asymmetric and symmetric stretching frequencies are obtained. The tetrahydrate complex shows  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  frequencies at 1624 and 1405  $\text{cm}^{-1}$  respectively, whereas in anhydrous complex, these frequencies are observed at 1629 and 1404  $\text{cm}^{-1}$  respectively. In nitrilotriacetic acid,  $\nu(\text{CN})$  absorption band is obtained at 1333  $\text{cm}^{-1}$  which lowers in case of metal complexes. The  $\nu(\text{NH})$  absorption band in hippuric acid is obtained at 3342  $\text{cm}^{-1}$  which in tetrahydrate complex appears at 3313  $\text{cm}^{-1}$ . In hippuric acid, amide I  $\nu(\text{C}=\text{O})$ , amide II  $\delta(\text{NH}) + \nu(\text{CN})$  with benzene ring vibrations and amide III  $\nu(\text{CN}) + \delta(\text{NH})$  bands are obtained at 1604, (1556, 1488 and 1416) and (1334, 1303)  $\text{cm}^{-1}$ , respectively. In metal complexes, the amide I band, amide II band and benzene ring vibrations are mixed together to give a composite broad band at *ca.* 1560  $\text{cm}^{-1}$ . Amide III band is mixed with

$\nu(\text{CN})$  vibrations and is obtained at 1308 and 1295  $\text{cm}^{-1}$  in tetrahydrate and anhydrous complexes respectively.  $\delta(\text{HOH})$  frequency is mixed with  $\nu_{\text{asym}}(\text{COO}^-)$  frequency and is observed at 1624  $\text{cm}^{-1}$ . Besides, tetrahydrate complex also shows additional band at *ca.* 3417  $\text{cm}^{-1}$  attributable to water molecules<sup>6</sup>. The IR frequencies for the ligands and metal complexes are given in Table-1.

TABLE-1  
IR FREQUENCIES ( $\text{cm}^{-1}$ ) OF HIPPURIC ACID, NITRILOTRIACETIC ACID  
AND THEIR TETRAHYDRATE AND ANHYDROUS MIXED  
LIGAND COPPER(II) COMPLEXES

Hippuric acid	Nitrilo-triacetic acid	$\text{Na}_2[\text{Cu}(\text{HA})\text{-(NTA)}]\cdot 4\text{H}_2\text{O}$	$\text{Na}_2[\text{Cu}(\text{HA})\text{-(NTA)}]$	Band assignment
—	—	3417	—	$\nu(\text{OH})$
3342	—	3313	—	$\nu(\text{NH})$
3075	3043, 2993	2930	—	$\nu(\text{CH})$
—	—	—	3415	$\nu(\text{NH}) + \nu(\text{CH})$
1746	1731	—	—	$\nu(\text{CO})$ carboxylic acid group
—	—	1624*	1629	$\nu_{\text{asym}}\text{COO}^-$
—	—	1405	1404	$\nu_{\text{sym}}\text{COO}^-$
1604	—	—	—	$\nu(\text{C}=\text{O})$ amide I band
1556, 1488, 1416	—	1564†	1561†	$\delta(\text{NH}) + \nu(\text{CN})$ amide II and benzene ring
1334, 1303	1333	1308‡	1295‡	$\nu(\text{CN})$ and ( $\nu\text{CN} + \delta\text{NH}$ ) amide III

\*  $\delta(\text{HOH})$  is mixed with  $\nu_{\text{asym}}(\text{COO}^-)$ .

† Amide I, amide II bands and benzene ring vibrations are mixed together to give a composite broad band at *ca.* 1560  $\text{cm}^{-1}$ .

‡  $\nu(\text{CN})$  and amide III band are mixed together.

It may thus be concluded that in copper(II) complexes, nitrilotriacetic acid coordinates through three carboxylate oxygen atoms and the nitrogen atom hence acts as a tetradentate ligand. Hippuric acid shows bidentate behaviour and the coordination occurs through carboxylate oxygen and the nitrogen of the amido group.

#### Magnetic studies and electronic spectra

The normal magnetic moment of copper(II) complexes,  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CO-NHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}]\cdot 4\text{H}_2\text{O}$ :  $\mu_{\text{eff}} = 1.90$  BM and  $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_5\text{CO-NHCH}_2\text{COO})\{\text{N}(\text{CH}_2\text{COO})_3\}]$ :  $\mu_{\text{eff}} = 1.73$  BM suggest a spin-free octahedral structure for the complexes<sup>7</sup>, which is supported by their electronic spectra<sup>8</sup>. The bands observed at 13680 and 13784  $\text{cm}^{-1}$  in tetrahydrate and anhydrous complexes respectively should be regarded for d-d transitions. Copper(II) complexes also show a band at 43956  $\text{cm}^{-1}$  which should be regarded as a charge transfer from the carboxylate group to the metal<sup>9</sup>. The values are given in Table-2.

TABLE-2  
MAGNETIC MEASUREMENTS AND ELECTRONIC SPECTRA  
FOR COPPER(II) COMPLEXES

Complex	Magnetic measurements					Electronic spectra	
	Temp (K)	$\chi_E \times 10^{-6}$ (cgs)	$\chi_M \times 10^{-6}$ (cgs)	$\chi_M' \times 10^{-6}$ (cgs)	$\mu_{\text{eff}}$ (BM)	d-d transition ( $\text{cm}^{-1}$ )	CT from L $\rightarrow$ M ( $\text{cm}^{-1}$ )
$\text{Na}_2[\text{Cu}(\text{HA})(\text{NTA})] \cdot 4\text{H}_2\text{O}$	292.0	2.6148	1432.81	1546.18	1.90	13680	43956
$\text{Na}_2[\text{Cu}(\text{HA})(\text{NTA})]$	284.5	2.4378	1160.10	1273.47	1.73	13784	43956

### NMR Studies

In hippuric acid and nitrilotriacetic acid, signals due to  $-\text{CH}_2$  protons are observed at 4.09 and 3.69 ppm, respectively. The signals for aromatic ring protons of hippuric acid in DMSO have been reported at 7.53 and 7.91 ppm<sup>10</sup>. In  $\text{CH}_3\text{OH}$ , hippuric acid shows signals for aromatic protons at 7.52 and 7.86 ppm. Signals for  $-\text{COOH}$  group are expected to appear beyond 10 ppm (10.5–12.0) ppm, hence could not be observed. Besides, NMR spectra also show signals for the solvent, methyl alcohol, at  $\delta$  value 3.31 ( $-\text{CH}_3$ ) and in the 4.84–4.91 ppm ( $-\text{OH}$ ) range.

In copper(II) complexes, signals only pertaining to aromatic protons are observed at *ca.* 7.45 ppm. The other signals corresponding to  $-\text{CH}_2$  groups of nitrilotriacetic acid and hippuric acid are so broadened by the proximity of the paramagnetic Cu(II) ion that it is no longer observable<sup>11,12</sup>. Thus it shows that the aromatic protons are far placed from the sites of the coordination, hence are not much affected. The coordination mainly occurs through the  $-\text{COOH}$  group of nitrilotriacetic acid and hippuric acid. Assignments<sup>11, 13, 14</sup> of NMR data for the ligands and the complexes are given in Table-3.

TABLE-3  
ASSIGNMENT OF  $^1\text{H}$  NMR DATA FOR LIGANDS AND COPPER(II) COMPLEXES

Compound	Medium	$\delta(\text{ppm})$	Assignment
Nitrilotriacetic acid	$\text{CH}_3\text{OH}$	3.69	$-\text{CH}_2$
Hippuric acid	$\text{CH}_3\text{OH}$	4.09, 7.52, 7.86	$-\text{CH}_2$ Aromatic protons
$\text{Na}_2[\text{Cu}(\text{HA})(\text{NTA})] \cdot 4\text{H}_2\text{O}$	$\text{CH}_3\text{OH}$	7.44	Aromatic protons
$\text{Na}_2[\text{Cu}(\text{HA})(\text{NTA})]$	$\text{CH}_3\text{OH}$	7.45	Aromatic protons

HA and NTA stand for anions of hippuric acid and nitrilotriacetic acid respectively.

### Conclusion

The evidences obtained from the above studies suggest a six-fold octahedral structure for the mixed ligand copper(II) complexes in which nitrilotriacetic acid acts as a tetradentate ligand and hippuric acid as a bidentate ligand (Fig. 1).

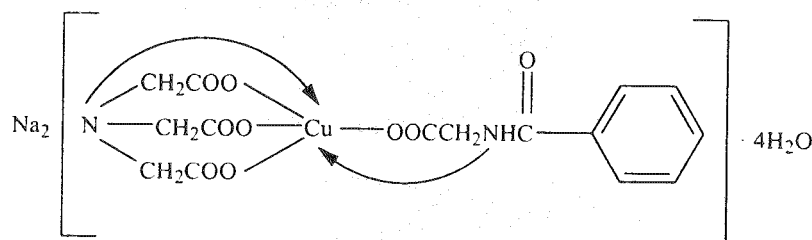


Fig. 1. Structure of hydrated copper(II) complex

### ACKNOWLEDGEMENTS

One of the authors (GK) is grateful to Prof R.R.T. Majinda, Head, Chemistry Department, University of Botswana, Gaborone, Botswana for providing the necessary research facilities. The author also gratefully acknowledges the financial support from the Research and Publications Committee of the Faculty of Science, University of Botswana, for the research project entitled "Studies on metal chelates and complexes of biological significance".

### REFERENCES

1. H. Sigel, *Metal Ions in Biological Systems: Mixed Ligand Complexes*, Vol. 2, Marcel-Dekker Inc., New York (1973).
2. N.B. Nigam, P.C. Sinha and M.N. Srivastava, *Indian J. Chem.*, **22A**, 218 (1983); **24A**, 893 (1985).
3. N.P. Singh, M.N. Srivastava and G. Kumar, *Orient. J. Chem.*, **16**, 223 (2000); *Tanz. J. Sci.*, **16**, 111 (1990).
4. M. Gupta and M.N. Srivastava, *Polyhedron*, **4**, 475 (1985); *Bull. Soc. Chem.(France)*, **128**, 859 (1991); *Bull. Pol. Acad. Sci.*, **40**, 227 (1992); *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 305 (1996).
5. G. Kumar and M.N. Srivastava., *Res. J. Chem. Environ.*, **9**, 43 (2005).
6. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn., Wiley-Interscience, New York (1966).
7. B.N. Figgis and J. Lewis, *The Magnetochemistry of Complex Compounds* in: J. Lewis and R.G. Wilkins (Eds.), *Modern Coordination Chemistry*, Interscience Publishers Company, New York (1960).
8. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company, New York (1968).
9. C.R. Hare, in: K. Nakamoto and P.J. MacCarthy (Eds.), *Visible and Ultraviolet Spectroscopy of Metal Chelate Compounds*, John Wiley & Sons Inc., New York (1968).
10. S.A. Sadeek, M.S. Refat, S.M. Teleb and S.M. El-Megharbel, *J. Mol. Struct.*, **737**, 139 (2005).
11. V.K. Saxena and M.N. Srivastava, *J. Inorg. Biochem.*, **38**, 37 (1990).
12. R. Mathur and N.C. Li, *J. Am. Chem. Soc.*, **86**, 1289 (1964).
13. J.R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, India (1971).
14. R.T. Morrison and R.N. Boyd, *Organic Chemistry*, 4th Edn., Allyn & Bacon Inc. (1983); Indian Reprint (1985).