

## Synthesis and Spectral Studies of Cu(II) Coordination Compounds of 4[N-(cinnamalidene) amino] Antipyrine Semicarbazone

LAKSHMAN SINGH\*, DEEPAK KUMAR SHARMA, UPMA SINGH  
and ALOK KUMAR†

*Department of Chemistry, Lajpat Rai Post Graduate College, Sahibabad-101 005, India.*

A series of five coordination compounds of copper(II) with 4[N-(cinnamalidene) amino] antipyrine semicarbazone (CAPS) has been described in this work. Characterization of these coordination compounds were made on the basis of elemental analysis, molecular weight, magnetic moment, conductivity measurements, infrared and electronic spectra. In all the coordination compounds CAPS behaves as tridentate (N,N,O) ligand. Thermal properties of these compounds were also investigated.

**Key Words:** Copper(II), Complexes, Semicarbazone.

### INTRODUCTION

In continuation of our work on bio-active metal coordination compounds of biologically active ligands<sup>1-3</sup>, here we report the synthesis and characterization of five coordination compounds of copper(II) with [4N-(cinnamalidene) amino] antipyrine semicarbazone (CAPS).

### EXPERIMENTAL

Copper(II) salts were obtained from BDH and used as such,  $\text{Cu}(\text{SCN})_2$  was prepared by mixing copper(II) chloride (in ethanol) and the ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having  $\text{Cu}(\text{SCN})_2$  was used immediately for complex formation. The ligand CAPS was prepared as reported earlier<sup>4</sup>.

All the coordination compounds were synthesized by following the general method. The corresponding copper(II) salt and CAPS were dissolved separately in ethanol and mixed with drop by drop. The reaction mixture was boiled under reflux for 2–3 h. On cooling and filtration, a microcrystalline compound separated out; the crystals were washed with ethanol and diethyl ether and kept in a desiccator over fused  $\text{CaCl}_2$ .

\*Corresponding author: H. No. 285A, Gali No. 4, Shyam Park (Main), Sahibabad-201 005, Ghaziabad, India. Tel: +91-0120-2624264; E-mail: deepak\_dks77@rediffmail.com

†Department of Chemistry, D.N. College, Meerut, India.

All the physico-chemical analyses were performed according to the reported method<sup>5, 6</sup>.

## RESULTS AND DISCUSSION

The reaction of Cu(II) salts with CAPS resulted in the formation of the coordination compounds  $[\text{Cu}(\text{CAPS})\text{X}\cdot\text{H}_2\text{O}]\text{X}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NCS}^-$  or  $\text{CH}_3\text{COO}^-$ ). The analytical data of these compounds are presented in Table-1. All the coordination compounds are quite stable and can be stored for months without any appreciable change. The compounds do not have sharp melting points but decomposed beyond 250°C. The molar conductance values of the copper(II) complexes in nitrobenzene (Table-1) indicate that they are 1 : 1 electrolytes. The molecular weights in the freezing nitrobenzene are in broad agreement with the conductance data (Table-1). The observed magnetic moments of the present compounds (Table-1) lie in the range 1.76–1.87 B.M. The observed magnetic moments of the complexes are inconsistent with the presence of a single unpaired electron.

TABLE-1  
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC  
MOMENT DATA OF COPPER(II) COORDINATION COMPOUNDS OF CAPS

Complex	% Analysis found (calculated)			m.w. found (calcd.)	$\Omega_m$ (ohm <sup>-1</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)
	Cu	N	Anion			
$\text{CuCl}_2(\text{CAPS})(\text{H}_2\text{O})$	11.96 (12.06)	15.80 (15.95)	13.36 (13.48)	262 (526.5)	24.1	1.76
$\text{CuBr}_2(\text{CAPS})(\text{H}_2\text{O})$	10.17 (10.31)	13.59 (13.64)	25.14 (25.99)	306 (615.5)	22.8	1.79
$\text{Cu}(\text{NO}_3)_2(\text{CAPS})(\text{H}_2\text{O})$	10.82 (10.95)	19.14 (19.32)	—	288 (579.5)	24.9	1.80
$\text{Cu}(\text{NCS})_2(\text{CAPS})(\text{H}_2\text{O})$	10.86 (11.47)	19.39 (19.59)	20.07 (20.29)	284 (571.5)	25.8	1.82
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{CAPS})(\text{H}_2\text{O})$	10.82 (11.07)	14.50 (14.64)	—	285 (573.5)	26.2	1.84

A study and comparison of IR-spectra of CAPS and its coordination compounds with copper(II) imply that the ligand behaves as a neutral tridentate coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms. The key infrared bands ( $\text{cm}^{-1}$ ) of these coordination compounds are presented in Table-2. the characteristic absorption of the carbonyl group in free CAPS is observed<sup>7</sup> at *ca.* 1700  $\text{cm}^{-1}$  (amide-I band). In all the coordination compounds, this band is shifted toward lower energy in 1650–1640  $\text{cm}^{-1}$  region. The amide-II band in CAPS has been observed at 1560  $\text{cm}^{-1}$ . In all the present coordination compounds, this band is also shifted towards lower wavenumbers by 25–30  $\text{cm}^{-1}$ .

This observation suggests coordination through the carbonyl oxygen atom. The strong band at *ca.* 1600  $\text{cm}^{-1}$  apparently has a large contribution from the  $\nu(\text{C}=\text{N})$  mode of semicarbazone moiety. This has been observed as a blue shift in the position of the  $\nu(\text{C}=\text{N})$  band in all the complexes as compared to the free ligand. Another strong band was observed at *ca.* 1620  $\text{cm}^{-1}$  due to azomethinic ( $\text{C}=\text{N}$ ) absorption. On complexation, this band is shifted towards the lower frequency region which is suggestive of the coordination through the azomethinic N-atom<sup>8</sup>. In far infrared spectra  $\nu(\text{Cu}-\text{N})/\nu(\text{Cu}-\text{O})$  bands have also been identified<sup>9</sup>. The presence of coordinated water was suggested by the broad adsorption band centred around 3440  $\text{cm}^{-1}$  in the infrared spectra. Bands at *ca.* 930 and 770  $\text{cm}^{-1}$  may be attributed to rocking and wagging modes of the coordinated water<sup>9</sup>.

TABLE-2  
KEY INFRARED BANDS ( $\text{cm}^{-1}$ ) OF COPPER(II) COORDINATION  
COMPOUNDS OF CAPS

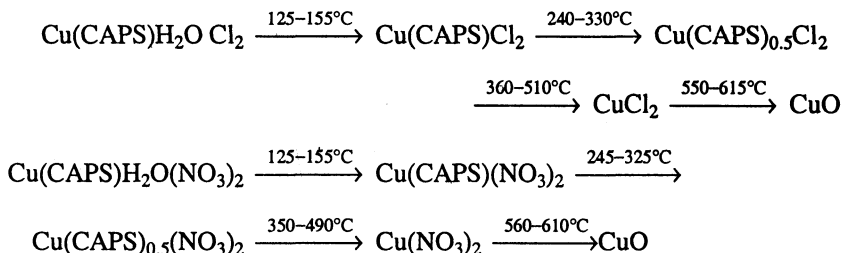
Assignments compounds	$\nu(\text{C}=\text{N})$ (azo- methinic)	$\nu(\text{C}=\text{N})$ (hydr- azinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{Cu}-\text{N})/\nu(\text{Cu}-\text{O})$
			I	II	III	
CAPS	1610 s	1600 s	1700 s	1572 m	1350 m	—
$\text{CuCl}_2(\text{CAPS})(\text{H}_2\text{O})$	1582 s	1622 s	1650 s	1535 m	1335 m	460 m, 390 w
$\text{CuBr}_2(\text{CAPS})(\text{H}_2\text{O})$	1590 s	1630 s	1645 s	1532 m	1330 m	450 m, 395 w
$\text{Cu}(\text{NO}_3)_2(\text{CAPS})(\text{H}_2\text{O})$	1585 s	1620 s	1640 s	1535 m	1332 m	450 m, 390 w
$\text{Cu}(\text{NCS})_2(\text{CAPS})(\text{H}_2\text{O})$	1583 s	1625 s	1652 s	1533 m	1335 m	440 m, 385 w
$\text{Cu}(\text{CH}_3\text{COO})_2(\text{CAPS})(\text{H}_2\text{O})$	1580 s	1628 s	1645 s	1535 m	1332 m	440 m, 380 w

In the infrared spectra of thiocyanate complex, the three fundamental absorptions ( $\text{C}-\text{N}$ ) stretch ( $\nu_1$ ), ( $\text{C}-\text{S}$ ) stretch ( $\nu_3$ ) and ( $\text{N}-\text{C}-\text{S}$ ) bending ( $\nu_2$ ) are identified, which are associated with the terminal N-bonded isothiocyanate ions<sup>10</sup>. The absence of  $\nu_3$  band of ionic nitrate ( $\text{D}_{3h}$ ) at *ca.* 1360  $\text{cm}^{-1}$  and the occurrence of two strong bands at 1520 and 1300  $\text{cm}^{-1}$  suggest the covalency of  $\text{NO}_3^-$  in  $\text{Cu}(\text{NO}_3)_2 \cdot (\text{CAPS})(\text{H}_2\text{O})$ . By applying Lever separation method<sup>11</sup>, the monodentate nature of  $\text{NO}_3^-$  in this complex is suggested. In acetate complex, two bands have been observed at *ca.* 1630 and 1390  $\text{cm}^{-1}$  which may be assigned to antisymmetric and symmetric ( $\text{COO}^-$ ) stretching vibrations respectively<sup>12</sup>.

The electronic spectra of Cu(II) complexes consist of a broad band in  $16000 \pm 200 \text{ cm}^{-1}$  range of medium intensity in the visible region which can be identified as a *d-d* band of the central ion, *i.e.*, an electronic transition mainly localized on Cu(II). Ligand field parameter *ca.* 10 Dq has been estimated from the equation suggested by Lever *et al*<sup>11</sup>. These data are in good agreement with those reported for other  $\text{D}_{4h}$  symmetry complexes.

Thermal properties of these complexes were studied by T.G.A.. The T.G. data indicate that the complexes contain one mole of coordinated water, which is

evident by loss of weight at *ca.* 155°C. There is no change up to *ca.* 250°C, after which there is a break in the curves due to évaporation of 0.5 mole of organic ligand; the remaining 0.5 mole of ligand is removed from the coordination sphere at *ca.* 510°C. Finally, at *ca.* 620°C, CuO is formed. Thermal equations are shown as below:



### ACKNOWLEDGEMENTS

The authors are thankful to Dr. S.D. Kaushik (Principal) and Dr. S.K. Agarwal, (Head, Chemistry Department) Lajpat Rai Postgraduate College, Sahibabad for their keen interest in the work.

### REFERENCES

1. L. Singh, P. Gupta and I. Chakarborti, *Asian J. Chem.*, **13**, 682 (2001).
2. L. Singh, P. Gupta, Upma and I. Chakarborti, *Asian J. Chem.*, **13**, 740 (2001).
3. L. Singh, P. Gupta and I. Chakarborti, *Asian J. Chem.*, **13**, 1363 (2001).
4. R.K. Agarwal, H. Agarwal and A.K. Manglik, *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 1163 (1996).
5. R.K. Agarwal, P. Agarwal, H. Agarwal and S.K. Gupta, *Synth. React. Inorg. Met.-Org. Chem.*, **28**, 251 (1998).
6. J.R. Chopra, D. Uppal, U.S. Arora and S.K. Gupta, *Asian J. Chem.*, **12**, 1277 (2000).
7. M.J.M. Campbell and R. Grzeskwiak, *J. Inorg. Nucl. Chem.*, **30**, 1865 (1968).
8. R.K. Agarwal and R.K. Sarin, *Polyhedron*, **12**, 2411 (1993).
9. D.M. Adam, *Metal-Ligand and Related Vibrations*, Arnold, London (1967).
10. J.L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1960).
11. ———, *Coord. Chem. Rev.*, **3**, 225 (1968).
12. A.B.P. Lever and B.S. Ramaswamy, *J. Chem. Soc.*, 5042 (1963).
13. K. Nakamoto, J.Y. Morimoto and A.E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).

(Received: 15 April 2003; Accepted: 20 November 2003)

AJC-3237