Asian Journal of Chemistry Vol. 4, No. 3 (1992), 652-654

NOTE

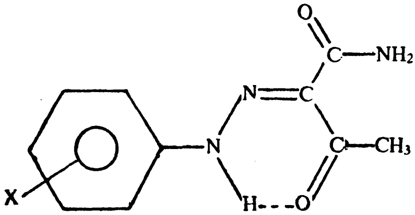
Studies on Complex Arylhydrazones. Part-VI

N. PRASAD*, A. SAHAY AND A. K. SRIVASTAVA

Chemical Laboratory, Department of Chemistry
L. S. College, Muzaffarpur-842 001, India

Cu(II) complexes with 2,3-dioxobutyramide-2-phenylhydrazone have been investigated by means of physico-chemical methods which include analytical, spectral (IR and electronic) and magnetic moment measurements. The results obtained from such measurements have led to the elucidation of their structures and revelation of the nature of M–L bonding present therein.

In present investigation Cu(II) complexes were isolated with 2,3-dioxobutyramide-2-phenylhydrazone and four related substituted phenylhydrazones (I)



During the complexation of Cu(II) ion with ethyl-2,3-dioxobutyrate-2-phenylhydrazones as ligand, in some cases compounds were isolated in which conversion of ester part into amide part followed by complexation were observed[1]. It was due to maintaining pH by NH_4OH and refluxing the mixture for a longer time. Therefore it was thought proper to prepare amide of ethyl-2,3-dioxobutyrate-2-phenylhydrazone and synthesis metal complexes using these amidic hydrazones as ligand. The results of such investigation is described in this paper.

Ethyl 2,3-dioxobutyrate-2 phenylhydrazones were prepared by adopting the procedure described earlier[2]. All ligands were synthesised by keeping ethanolic solution of ethyl 2,3-dioxobutyrate-2-phenylhydrazone for 3–4 days in NH_4OH.

An alcoholic solution of ligand was mixed with an alcoholic solution of copper(II) acetate in equimolar ratio and the pH of the resulting mixture was maintained 8 by adding NH_4OH. The mixture was refluxed on water bath for 5–8 hrs. The separated insoluble product was filtered, washed first with water and finally with hot benzene. All complexes were carefully recrystallised with nitrobenzene and dried over fused $CaCl_2$ (yield, 40–60%). Absence of free ligand was ascertained by TLC examination.

Analytical data are approximately ± 2% error and favour ML_2 stoichiometry for all complexes having general composition $[CuL_2 \cdot 2H_2O]$. These complexes are non-hygroscopic and instable. The complexes are insoluble in water and in common organic solvents but they partially dissolve in warm $PhNO_2$ and DMSO. The magnetic moment of the complexes lie in the range 1.88–1.96 BM. These values correspond to one unpaired spin. From the observed magnetic moment value (Table 1) it is evident that the complexes are magnetically dilute i.e. there is no antiferromagnetic coupling between adjacent Cu(II) ion at room temperature.

TABLE 1

MAGNETIC MOMENT, PHYSICAL CONSTANTS AND ANALYTICAL DATA OF COMPLEXES

Name of Complex	μ_{eff} (in B.M.) (at 298°K)	Decomposition temp. (°C)	% yield	Colour	N% Found (calcd)	Cu% Found (calcd)
$[Cu(L_1)_2 \cdot 2H_2O]$	1.91	>280	61	Greenish Grey	16.55 (16.72)	12.37 (12.51)
$[Cu(L_2)_2 \cdot 2H_2O]$	1.88	>280	56	Grey	18.43 (18.74)	10.41 (10.62)
$[Cu(L_3)_2 \cdot 2H_2O]$	1.96	212	40	Yellowish Grey	15.43 (15.68)	11.52 (11.85)
$[Cu(L_4)_2 \cdot 2H_2O]$	1.89	270	55	Yellowish Grey	15.35 (15.68)	11.43 (11.85)
$[Cu(L_5)_2 \cdot 2H_2O]$	1.92	270	65	Grey	12.35 (12.62)	9.13 (9.54)

The diffuse reflectance spectra of Cu(II) complexes display two weak and broad ligand field transitions in the vicinity of 20,000–20,400 cm^{-1} and 15,000–16,000 cm^{-1} similar to tetragonally distorted octahedral complexes. These bands are probably due to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively[3].

All Cu(II) complexes display a broad band at around 3400–3500 cm^{-1} attributed to ν_{O-H} of water[4]. The three (N–H) stretching vibrations of ligand molecules are observed in the region 3060–3080 cm^{-1}, 3150–3190 cm^{-1} and 3200–3300 cm^{-1} as medium bands. The bands in the region 3150–3190 cm^{-1} and 3200–3300 cm^{-1} are assigned as a (N–H) stretching vibration of amide group; however, the red shifted (N–H) stretching vibration (3060–3080 cm^{-1}) in present set of ligand molecules can be attributed to ν_{N-H} of hydrogen bonded phenylamino group. Unlike ligand molecule, Cu(II) complexes display only two (N–H) stretchings at around 3120–3190 cm^{-1} and 3200–3280 cm^{-1}. The disappearance of hydrogen bonded ν_{N-H} indicates its deprotonation and involvement of deprotonated phenylamino nitrogen in coordination. In some complexes ν_{O-H} and ν_{N-H} vibration could not be separated probably due to their coupling and yielded a broad hump in the region 3100–3500 cm^{-1}. No appreciable change in $\nu_{C=O}$ vibration of amide part (observed at 1665–1670 cm^{-1} in ligands) is observed in complexes. A band observed at around 1640 cm^{-1} in the spectrum of ligand is assigned as $\nu_{C=O}$ vibration of hydrogen bonded carbonyl group. This band gets shifted in low frequency region at around 1620 cm^{-1} in the spectra of complexes which suggests that the O atom of hydrogen bonded carbonyl group is now involved in complexation. $\nu_{C=N}$ frequencies (observed at 1600 ± 10 cm^{-1} in ligand) remain almost at the same position in the spectra of all complexes. In far IR region, all complexes display two to three extra bands located around 510–480 cm^{-1} and 410–430 cm^{-1} attributed to ν_{Cu-O} and ν_{Cu-N} stretches respectively[4].

The complexes are stable at room temperature and do not lose weight below 150°C indicating that water molecules are involved in coordination. After heating over 150°C, the loss of weight was started with gradual change in colour indicating loss of coordinated water molecules from complex. All complexes decomposes finally at about 280°C (Table 1).

ACKNOWLEDGEMENTS

The authors are thankful to C.D.R.I., Lucknow; R.S.I.C., I.I.T., Bombay and R.S.I.C., I I.T., Madras for analytical and spectral measurements. Thanks are also due to Prof. L. K. Mishra, Patna Science College, Patna for magnetic moment measurements and valuable suggestions.

REFERENCES

1. A. Sahay, Ph.D. Thesis, Bihar University, Muzaffarpur (1989).
2. H. J. Barber, K. Washbounne, W. R. Wragg and E. Lunt, *J. Chem. Soc.*, 2828 (1961).
3. H. Elliott and B. J. Hathaway, *Inorg. Chem.*, 5, 887 (1966).
4. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1978).

(*Received*: 27 July 1990; *Accepted*: 15 January 1991) AJC-325