Asian Journal of Chemistry Vol. 10, No. 1 (1998), 46–49

Indicator Absorbance Spectra and Ligand Complexation Ratio with Metal Ions

RAKESH FARASRAM†, P.L. FARASRAM* and C.M. DESAI‡
Chemistry Department
Shri Jayendrapuri Arts and Science College, Bharuch-392 002, India

Three reagents β-arylaminocrotonophenylhydrazides were prepared and their ML and ML_2 complexes of copper(II) and mercury(II) ions were prepared. Their compositions were studied by usual methods. Spectrophotometric study can only be employed for coloured complexes by Job, Mole ratio and slope ratio methods. In this communication spectrophotometic study of above complexes was done by a novel dye indicator method for composition study of coloured copper complex and colourless mercury complex by monovariation method.

INTRODUCTION

Farasram *et al.*[1] has employed dye indicators for the investigation of complex ions formation between lead nitrate and alkalinitrate in water; however, these complex ions are unstable. Farasram[2] has also investigated the chelate formation between metal ions and ligands and used spectrophotometric methods—Job, slope ratio and mole ratio methods—for the study of complexes formed by the ligands with copper(II) ions, but these methods can only be employed for composition of coloured complexes such as copper but not with mercury which does not form coloured complexes. However, this novel indicator method has been used for investigation of composition of number of complexes between ligand and both metal ions in the present work.

The present communication also deals with the preparation of complexes of ML and ML_2 type of copper(II) and mercury(II) ions with the reagents β-*p*-chloroanilinocrotonophenylhydrazide (*p*-HCACPH), β-*p*-methylanilinocrotonphenylhydrazide (*p*-HMACPH) and β-*p*-nitroanilinocrotonophenylhydrazide (*p*-HNACPH) and their compositions were studied by usual methods.

EXPERIMENTAL

Ethyl-β-arylaminocrotonates were prepared by condensing *p*-chloroaniline, *p*-toluidine and *p*-nitroaniline with ethylacetoacetate by the known methods.[3] β-Arylaminocrotonophenylhydrazides were prepared by refluxing equimolar mixture of crotonate and phenylhydrazine on a water bath for 1/2 h and the reaction mass was then leached with hydrochloric acid (5%), saturated sodium chloride, water and then extracted with anhydrous ether; evaporation of ether gave the pure product.[4, 5]

---

*P.L. Farasram, 866, Muktınagar, G.H.B., Bharuch-392 001, India.

†Jr. Lab. Technician, Gujarat Narmada Valley Fertilizers Company Limited, Narmadanagar, 392 015, Distt. Bharuch, India.

‡Themis Chemicals Ltd, Vapi, India.

ML and ML_2 type complexes of copper and mercury were prepared by stirring for 1 h, at room temperature, mixture of methanolic solution of metal chloride (0.03 M; 25 mL) and methanolic solution of reagent (0.03 M; 15 mL) for ML type addition complexes and methanolic solution of metal chloride (0.03 M; 10 mL) and methanolic solution of the reagent (0.03 M; 40 mL) at pH 7 to 7.5 for ML_2 type covalent complexes when fine crystals of the complexes separated out. ML type complexes were washed with methanol and anhydrous ether. ML_2 type complexes were washed with methanol for purification.

ML complexes were microcrystalline solids, soluble in alcohol and insoluble in other. They were soluble with decomposition in hydrochloric acid. They have high melting points. The copper complexes were brown and the mercury complexes were yellowish white in colour.

ML_2 complexes were also microcrystalline solids. They were insoluble in water, alcohol and chloroform and soluble in dioxane and dimethylformamide. The copper complexes were brown and mecury complexes were yellowish white in colour.

RESULTS AND DISCUSSION

The molecular formulae of these complexes were checked by elemental analyses. The following complexes were thus prepared, melting points of the complexes are reported here.

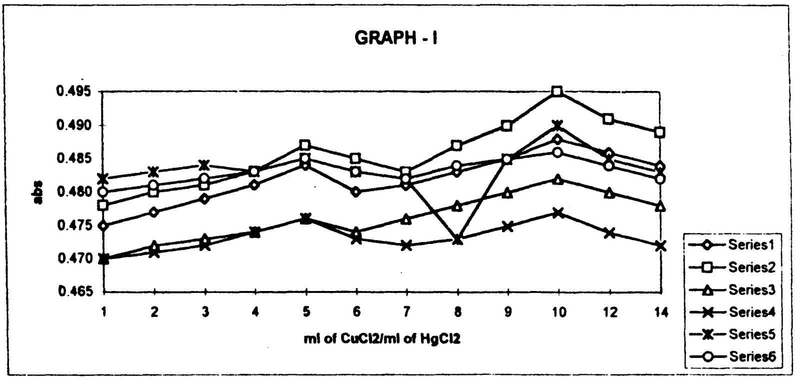
		m.p. (°C)
1.	*p*-HCACPHCu(II)Cl_2($C_{16}H_{16}N_3OCl_3Cu$)	> 310 d
2.	*p*-HMACPHCu(II)Cl_2($C_{17}H_{19}N_3OCl_2Cu$)	> 237 d
3.	*p*-HNACPHCu(II)Cl_2($C_{16}H_{16}N_4O_3Cl_2Cu$,)	> 275 d
4.	*p*-HCACPHHg(II)Cl_2($C_{16}H_{16}N_3OCl_3Hg$)	> 285 d
5.	*p*-HMACPHHg(II)Cl_2($C_{17}H_{19}N_3OCl_2Hg$)	> 242 d
6.	*p*-HNACPHHg(II)Cl_2($C_{16}H_{16}N_4O_3Cl_2Hg$)	> 275 d
7.	(*p*-CACPH)$_2$Cu(II)($C_{32}H_{30}N_6O_2Cl_2Cu$)	> 290 d
8.	(*p*-MACPH)$_2$Cu(II)($C_{34}H_{36}N_6O_2Cu$)	> 268 d
9.	(*p*-NACPH)$_2$Cu(II)($C_{32}H_{30}N_8O_6Cu$)	> 360 d
10.	(*p*-CACPH)$_2$Hg(II)($C_{32}H_{30}N_6O_2Cl_2Hg$)	> 230 d
11.	(*p*-MACPH)$_2$Hg(II)($C_{34}H_{36}N_6O_2Hg$)	> 243 d
12.	(*p*-NACPH)$_2$Hg(II)($C_{32}H_{30}N_8O_6Hg$)	> 260 d

d—decomposed.

The low molar conductance of ML_2 complexes of copper and mercury indicates the covalent nature of bonding. The effective magnetic moments of ML and ML_2 complexes of copper were normal and in the range 1.8 to 1.9 B.M. expected for planar stereochemistry.

A Shimadzu double beam spectrophotometer-160A was used for spectral study and was carried out by monovariation method using dye crystal violet (C.V.) as indicator. The absorbance of pure dye in methanolic solution was measured and absorbance at λ_{max} of the dye was taken as standard and the absorbance at λ_{max} in each case of dye-reagent-metal chloride system in methanol measured with increase in concentration of metalchloride, while keeping the concentration of the reagent constant using monovariation method, dye concentration being contant.[1] When such absorbance was plotted against increasing metal chloride concentration, the graphs indicate peaks corresponding to the complex formation in the ratio of concentration of metal and ligand in stoichiometric proportion for the system in 1 : 2 and 1 : 1 in graph-1 where the concentration of metal chloride was varying and reagent was constant. Hence it was concluded that in solution state also ML and ML_2 complexes were formed.

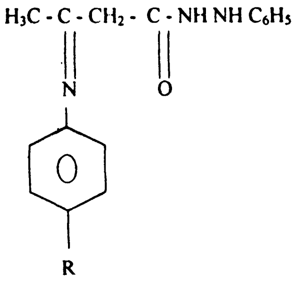
The strong band at *ca.* 1610 cm^{-1} and 1550 cm^{-1} in the spectra of ligands can be attributed to the unconjugated C=O and C=N groups respectively and they shift to higher frequency at *ca.* 1700 cm^{-1} and 1600 cm^{-1} in the infrared spectra of ML complexes. The increase in the frequency attributed to coordination through oxygen and nitrogen of C=O and C=N groups.[4, 5] In case of ML_2 complexes they shift to lower frequency at *ca.* 1600 cm^{-1} and *ca.* 1505 cm^{-1} as C—O stretch merging with C=C vibration band and suggesting coordination through the nitrogen of C=N group and formation of metal nitrogen bond.[6]



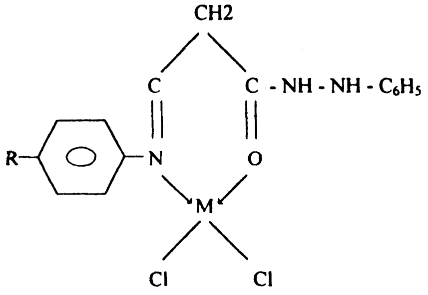
Series 1 . mL of M/50 $CuCl_2$+10 mL M/50 *p*-HCACPH + 5 mL of 5×10^{-5} M C.V
Series 2 mL of M/50 $CuCl_2$+10 mL M/50 *p*-HMACPH + 5 mL of 5×10^{-5} M C.V
Series 3 mL of M/50 $CuCl_2$+10 mL M/50 *p*-HNACPH + 5 mL of 5×10^{-5} M C.V
Series 4 mL of M/50 $HgCl_2$+10 mL M/50 *p*-HCACPH + 5 mL of 5×10^{-5} M C.V
Series 5 mL of M/50 $HgCl_2$+10 mL M/50 *p*-HMACPH + 5 mL of 5×10^{-5} M C.V
Series 6 mL of M/50 $HgCl_2$+10 mL M/50 *p*-HNACPH + 5 mL of 5×10^{-5} M C.V
C.V. = Crystal Violet.

The band due to CH_2 wagging vibrations located at *ca.* 1200 cm^{-1} in the spectra of ligands is absent in the spectra of complexes in which new bands appear at *ca.* 1280 cm^{-1} and *ca.* 760 cm^{-1} corresponding to the C—H in-plane bending and C—H out-of-plane bending vibrations. The shifting to lower frequency supports the enolisation of the ligand when complexation takes place in ML_2 complexes.[6] In all the ligands and complexes there is a band at *ca.* 1150 cm^{-1} corresponding to C—N stretching vibrations.[4, 5] There are two bands at *ca.* 3015 cm^{-1} and *ca.* 3035 cm^{-1} corresponding to unconjugated NH stretching bands indicating that nitrogen of the hydrazide is not taking part in complex formation.[4, 5] The bands appear at *ca* 3000 cm^{-1} corresponding to the symmetric and antisymmetric aromatic C—H stretching vibrations. The bands observed at *ca.* 2900 cm^{-1} are due to aliphatic C—H stretching vibrations.[6]

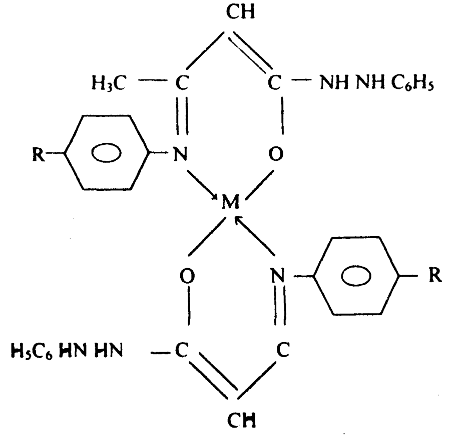
The studies of composition, spectrophotometric, magnetic moment, molar conductance and IR spectra confirm the following structures of ligands and complexes.



Ligand: β-arylaminocrotonophylhydrazide
(where R = —Cl, —CH_3 or —NO_2 group)



ML complex (Addition complex)
where M = Cu(II) and Hg(II)



ML_2 complex (M = Cu or Hg) (Covalent complex)

REFERENCES

1. P.L. Farasram, R. Farasram and C.M. Desai, Asian J. Chem., **9**, 758 (1997).
2. P.L. Farasram, M. Phil. Dissertation, South Gujarat University (1979).
3. A.C. Desai and C.M. Desai, *J. South Guj. Uni.*, **7**, 137 (1979); *J. Indian Chem. Soc.*, **54**, 1201 (1979).
4. P.D. Desai, A.G. Mehta and C.M. Desai, *J. South Guj. Uni.*, **9**, 105 (1980).
5. A.G. Mehta, *J. Inst. Chemists (India)*, **55**, 13 (1983).
6. J.N. Patil and D.N. Sen, *Indian J. Chem.*, **12**, 189 (1974).

(*Received*: 12 May 1997; *Accepted*: 3 September 1997) AJC-1333