

The author is thankful to Prof. B. Sanjeevaiah, Head of this Department, for encouragement and to Dr. B. N. Murthy for his interest in this work. He acknowledges his UGC Junior Research Fellowship awarded by the University of Mysore, Mysore.

Dept. of Post-Graduate Studies and Research in Physics,
University of Mysore,
Manasagangotri, Mysore 570 006,
India, March 10, 1976.

1. Herzberg, G., *Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules* (Second Edn.), (D. Van Nostrand, New York, 1950).
2. Fraser, P. A., *Can. J. Phys.*, 1954, 32, 515.
3. Mishra, P. K. and Khanna, B. N., *J. Quant. Spectrosc. Radiat. Transfer*, 1970, 10, 703.
4. Nicholls, R. W., *Can. J. Phys.*, 1954, 32, 722.

ADDUCTS OF BIS (ETHYLACETOACETATO) COPPER (II) WITH NITROGEN LIGANDS

BONDING¹⁻³ of additional ligands along the axis normal to the molecular plane of planar complexes like beta-diketonates and related compounds, which involve keto-enol tautomerism, have invoked a lot of interest in recent years. Since beta-keto esters are closely related to the beta-diketones, it was thought worthwhile to extend the investigation to such chelates and this communication reports some base adducts of bis-(ethyl acetoacetato copper (II) with substituted pyridines, viz., -2, 3- and 4-methyl pyridines.

Ethanol solution of cupric chloride was reacted with ethyl acetoacetate in (1 : 2) proportion, followed by dropwise addition of ammonia with constant stirring. The green product obtained was filtered off, washed with ethanol and ether and dried in a vacuum desiccator. Metal chelate and the nitrogen ligands (in 1 : 2 ratio) were taken in minimum quantity of ethanol and refluxed for thirty minutes. On cooling the solution overnight, crystalline compounds separated out.

Metal ion in the compounds was estimated by EDTA procedure. Conductance was measured in M/1000 acetone solution using a 'Toshniwal' conductance bridge. Magnetic susceptibility was measured on the solid specimen by Gouy method. Infrared spectra were recorded in nujol mulls with Unicam SP 200 Spectrophotometer. U.V. and visible spectra were recorded using M/100 chloroform-base solution in Unicam SP 500 Spectrophotometer. The relevant analytical, conductance and magnetic susceptibility data are recorded in Table I.

Results and Discussion

The green crystalline compounds have the composition $\text{Cu}(\text{EAA})_2\text{L}_2$ where 'L' is substituted pyridine. The compounds are stable in air, have low melting points. Acetone solutions of the complexes have low molar conductance values, Λ_M being in the range of 2-4 mhos, indicating non-electrolytic nature.

Most of the absorption bands due to the free nitrogen ligands are shifted in the adducts indicating bonding to the metal, information being obtained by the "Finger Print" technique. $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the ester which occur at 1650 and 1630 cm^{-1} respectively shift to lower frequency region (1600 and 1525 cm^{-1}) on chelation and again shift to higher frequency (1620 and 1540 cm^{-1} respectively) in the nitrogen base adducts providing additional evidence for bonding of the ester and nitrogen ligand. Direct evidence could not be obtained as $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$ were beyond the range of instrument used.

An intense band appeared in the U.V. region around 260 nm ($\epsilon = 15000$) in solution spectrum of the chelate and base adducts due to the more probable $\pi \rightarrow \pi^*$ transition rather than charge transfer. In the visible region, a broad absorption band was observed around 660 nm ($\epsilon = 60$) in the chelate which was found around 650 nm ($\epsilon = 85$) in the base adducts. On coordination of the nitrogen ligands there is not much shift in the position of the absorption band though the intensity increases.

TABLE I

Analysis, M.P., Conductance and magnetic susceptibility data of bis-(ethyl acetoacetato) Copper (II) complexes

Compounds	Colour and form	MP (°C)	Λ_M ohm ⁻¹ cm ²	μ_{eff} (B.M.)	% Metal		% N	
					Reqd.	Found	Reqd.	Found
$\text{Cu}(\text{EAA})_2(\alpha\text{-pic})_2$	Green crystalline	160	2.8	1.76	1.56	12.0	5.52	5.3
$\text{Cu}(\text{EAA})_2(\beta\text{-pic})_2$	do.	180	3.0	1.74	12.56	12.1	5.52	5.25
$\text{Cu}(\text{EAA})_2(\gamma\text{-pic})_2$	do.	175	4.2	1.78	12.56	11.9	5.52	5.32

This is in conformity with some earlier observations⁴. Hence the complexes are six-coordinated, presumably having a tetragonally distorted octahedral configuration. Though distorted octahedral Cu (II) complexes have three transitions ($2B_{1g} \rightarrow 2B_{2g}$, $2B_{1g} \rightarrow 2E_g$, $2B_{1g} \rightarrow 2A_{1g}$), often the three bands appear⁵ in a single broad asymmetric band envelope. The base adducts appear to be far more stable than their beta-diketonato analogues since in absence of the added base, there is no change in the position of absorption band in solution spectrum indicating "no appreciable dissociation" of the ligands.

Department of Chemistry,
Ravenshaw College,
Cuttack 3 (Orissa),
February 21, 1976.

N. C. MISHRA.
B. K. MOHAPATRA.
S. GURU.

1. Graddon, D. P., *Nature* (London), 1959, 183, 1610.
2. Walker, W. R., *Aust. J. Chem.*, 1961, 14, 161.
3. Gillard, R. D. and Wilkinson, G., *J. Chem. Soc.*, 1963, p. 5399.
4. Graddon, D. P. and Mockler, G. M., *Aust. J. Chem.*, 1968, 21, 907.
5. Agamber, C. A. and Orrel, K. G., *J. Chem. Soc. (A)*, 1969, p. 897.

BROMINATION OF ACETANILIDE CATALYSED BY ANHYDROUS FERRIC CHLORIDE, ANHYDROUS ZINC CHLORIDE AND IODINE BROMIDE

It is a common practice in synthetic organic chemistry to speed up the halogenation of aromatic compounds by the addition of halogen carriers such as iodine, iron powder, anhydrous halides of iron, zinc and aluminium, silver salts and pyridine^{1,2}. Iodine bromide has been shown to be the effective catalyst in the presence of added amounts of iodine in the bromination of aromatic compounds³⁻⁵.

In the presence of IBr, ZnCl₂ and NaCl as catalysts, the bromination of anisole in 85% aqueous acetic acid has been shown⁶ to proceed by simultaneous catalysed and uncatalysed processes. In the present investigation⁷, the bromination of acetanilide in the presence of added salts was followed kinetically³ at 30°C by mixing 5 ml each of 0.02 M solutions of acetanilide and bromine in anhydrous acetic acid, allowing them to react for definite intervals of time and arresting the reaction by the addition of 10 ml of an aqueous solution of 1.0 g of KI. In the FeCl₃-catalysed reaction, the KI solution also contained 0.33 g of NaF, which complexes with Fe³⁺ preventing the oxidation of KI by Fe³⁺.

In the absence of catalysts, the acetanilide-bromine reaction was found to be of the third order in the range 0.02–0.01 M. The individual orders determined by the isolation method³ were 1.0 for acetanilide and 1.9 for bromine, in agreement with recent work⁸. When anhydrous ferric chloride was added to the reaction mixture, there was an increase in the rate of the reaction. When the concentration of FeCl₃ in the reaction mixture was increased (3.6×10^{-4} to 54×10^{-4} M), there was a steady increase in the observed average third order rate constant for 20–50% bromine consumption. A similar catalysis was observed in the presence of added anhydrous ZnCl₂ and iodine (which forms iodine bromide *in situ*), as seen from Table I.

The rate of bromination of acetanilide in the presence of added salts (A) may be expressed as follows:

$$-\frac{d(\text{Br}_2)}{dt} = k(\text{ArH})(\text{Br}_2)^2 + k_e(\text{ArH})(\text{Br}_2)^2(\text{A})$$

or (1)

$$k_3 = k + k_e(\text{A}) \quad (2)$$

where k_3 is the observed third order rate constant, and k and k_e are the rate constants for the uncata-

TABLE I

Effect of added salts on the bromination of acetanilide

Acetanilide = 0.010 M		Solvent: Anhy. HOAc			
Bromine = 0.010 M		Temp. 30.0 ± 0.1°C			
FeCl ₃ × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)	ZnCl ₂ × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)	IBr × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)
3.6	3.73 ± 0.03	2.6	3.80 ± 0.04	0.8	3.78 ± 0.06
15.0	4.07 ± 0.04	5.3	4.07 ± 0.02	1.6	4.05 ± 0.10
32.7	4.53 ± 0.06	8.4	4.45 ± 0.03	2.9	4.55 ± 0.20
54.0	5.00 ± 0.05	16.6	5.34 ± 0.02	4.8	5.14 ± 0.38

All the concentrations quoted are those after mixing.