

Studies on Copper(II) Complexes with Arylazo-Bis-Acetoximes

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Copper(II) complexes with seven arylazo-bis-acetoximes have been synthesized, characterized by standard physico-chemical methods and their infra-red spectra have been taken. The studies revealed that arylazo-bis-acetoximes formed tetra coordinated complexes with copper(II). A square-planar geometry has been proposed for these copper(II) complexes.

Key Words: Copper(II) complexes, Arylazo bis-acetoximes.

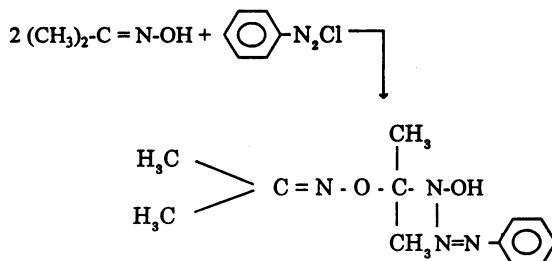
INTRODUCTION

Arylazo-bis-acetoximes (AABAs) are compounds possessing same chelating group as hydroxytriazenes. A number of hydroxytriazenes have been used for both spectrophotometric and complexometric determination of transition metals in our laboratory¹⁻⁶, but no AABAs have been used for the transition metal determination. Further, there are no studies on the solid complexes of AABAs with copper(II). In view of this seven AABAs have been synthesised using methods of Mai⁷ and their solid complexes with copper(II) have been prepared. An attempt has been made to study their infra-red spectra and predict geometries of the complexes on this basis.

EXPERIMENTAL

Synthesis of AABAs: As reported in the method of Mai⁷, AABAs are prepared by coupling an oxime with a diazonium salt in the ratio of 2 : 1 at 0°C in sodium hydroxide solution at pH close to 10.

A general reaction is presented by



Using the above method following seven AABAs have been prepared:

- (i) Phenylazo-bis-acetoxime
- (ii) *m*-Chloro phenylazo-bis-acetoxime
- (iii) *o*-Methyl phenylazo-bis-acetoxime
- (iv) *m*-Methyl phenylazo-bis-acetoxime
- (v) *p*-Bromo phenylazo-bis-acetoxime
- (vi) *o*-Carboxy phenylazo-bis-acetoxime
- (vii) *p*-Sulphonamido phenylazo-bis-acetoxime

Preparation of solid complexes: All the copper(II) complexes arylazo-bis-acetoximes were prepared by the following general method. A weighed quantity of each of the AABA was dissolved in minimum quantity of alcohol. In case of compound (VII), since it was not soluble in alcohol, it was dissolved in acetone. Copper sulphate pentahydrate (0.005 mole BDH AR grade) was weighed and dissolved in minimum quantity of double distilled water. pH of the reaction solution was maintained using 2% tris buffer. The metal solution was added dropwise to the solution of each AABA under constant magnetic stirring. After this the complete addition reaction mixture was further stirred for 5 min and was kept aside for 10 min. When the complex separated, it was filtered under suction. The product was washed with double distilled water and then with alcohol/acetone to remove unreacted metal as well as ligand. The product was recrystallised with alcohol and was finally dried in an oven at 100°C. Following this general procedure solid complexes of copper(II) of all the seven AABAs were prepared. The experimental details such as quantities and desired pH etc. have been incorporated in Table-1.

RESULTS AND DISCUSSION

Results of elemental analysis revealed that seven AABAs form 1 : 2 complexes with copper(II). The calculated values agree well with the experimental values (Table-2).

In AABAs, on the basis of the fact that they possess same basic skeleton as hydroxytriazenes four characteristic bands have been assigned (Table-3). Bands in the range 3625–3415 and 3350–3100 cm^{-1} have been assigned^{8,9} to $\nu(\text{OH})$ and $\nu(\text{NH})$ respectively. Similarly bands at $1070 \pm 9 \text{ cm}^{-1}$ have been assigned⁹ to $\delta(\text{NOH})$. This assignment has also been made on the basis of appearance of similar bands in hydroxylamines¹⁰.

However, on account of strong intramolecular hydrogen-bonding $\nu(\text{OH})$ may become very broad and as such have not been observed in all the seven AABAs.

Further, a band at $1520 \pm 10 \text{ cm}^{-1}$ may be assigned to $\delta(\text{NH})$. A similar assignment at 1520 cm^{-1} has been made in case of diazoaminobenzene ($\text{C}_6\text{H}_5\text{—NH—N=N—C}_6\text{H}_5$) by Kubler *et al.*¹¹

AABAs formed complexes by the removal of proton from this group —N=N—N—OH . It is expected that due to complex formation the characteristic bands of AABAs [$\nu(\text{NH})$, $\delta(\text{NOH})$ and $\delta(\text{NH})$] would disappear in the infrared spectra of solid complexes.

TABLE-1
SOLID COMPLEXES OF COPPER(II) WITH ARYL AZO-BIS-ACETOXIMES

S.No.	Name of reagent	pH	Reactants taken in molar proportion [Cu(II) : R]	Reagent (g)	Copper sulphate (g)	Amount of complex obtained (g)	yield (%)	Colour and shape of complex	m.p. (°C)
(I)	Phenylazo-bis-acetoxime	6.0-7.5	1 : 2	2.50	1.25	1.88	66.6	Dark green microcrystals	185
(II)	<i>m</i> -Chloro phenylazo-bis-acetoxime	6.2-7.4	1 : 2	2.85	1.25	2.06	65.0	Greenish yellow microcrystals	135
(III)	<i>o</i> -Methyl phenylazo-bis-acetoxime	6.0-7.0	1 : 2	2.64	1.25	2.40	81.0	Red microcrystals	110
(IV)	<i>m</i> -Methyl phenylazo-bis-acetoxime	5.6-7.9	1 : 2	2.64	1.25	2.40	81.0	Greenish yellow microcrystals	138
(V)	<i>p</i> -Bromo phenylazo-bis-acetoxime	5.0-7.0	1 : 2	3.28	1.25	2.78	77.2	Greenish yellow microcrystals	240
(VI)	<i>o</i> -Carboxy phenylazo-bis-acetoxime	7.0-8.0	1 : 2	2.94	1.25	2.08	63.8	Dark green microcrystals	140
(VII)	<i>p</i> -Sulphonamido phenylazo-bis-acetoxime	5.0-7.0	1 : 2	3.29	1.25	2.54	70.4	Canary yellow microcrystals	113

TABLE-2
ANALYTICAL DATA OF COPPER(II) COMPLEXES OF AABAs

S.No.	Copper(II) complex with	Elemental analysis % Found (Calcd.)			m.f.
		C	H	N	
(I)	Phenylazo-bis-acetoxime	50.60 (51.28)	6.07 (6.09)	19.24 (19.93)	Cu(C ₁₂ H ₁₇ N ₄ O ₂) ₂
(II)	<i>m</i> -Chloro phenylazo-bis-acetoxime	45.10 (45.68)	5.14 (5.11)	17.60 (17.75)	Cu(C ₁₂ H ₁₆ N ₄ O ₂ Cl) ₂
(III)	<i>o</i> -Methyl phenylazo-bis-acetoxime	53.10 (52.91)	6.51 (6.48)	19.20 (18.98)	Cu(C ₁₃ H ₁₉ N ₄ O ₂) ₂
(IV)	<i>m</i> -Methyl phenylazo-bis-acetoxime	52.96 (52.91)	6.49 (6.48)	18.79 (18.98)	Cu(C ₁₃ H ₁₉ N ₄ O ₂) ₂
(V)	<i>p</i> -Bromo phenylazo-bis-acetoxime	40.41 (40.04)	4.52 (4.48)	17.80 (17.56)	Cu(C ₁₂ H ₁₆ N ₄ O ₂ Br) ₂
(VI)	<i>o</i> -Carboxyl phenylazo-bis-acetoxime	48.00 (48.03)	5.21 (5.27)	17.50 (17.23)	Cu(C ₁₃ H ₁₇ N ₄ O ₄) ₂
(VII)	<i>p</i> -Sulphonamido phenylazo-bis-acetoxime	41.00 (40.02)	5.07 (5.03)	19.20 (19.44)	Cu(C ₁₂ H ₁₈ N ₅ O ₄ S) ₂

The key infrared bands of all the ligands are presented in Table-3.

TABLE-3
ASSIGNMENTS OF THREE CHARACTERISTIC BANDS (cm⁻¹) FOR ARYL
AZO-BIS-ACETOXIMES

S.No.	Name of the arylazo-bis-acetoximes	v(NH)	δ(NOH)	δ(NH)
(I)	Phenylazo-bis-acetoxime	3230 s	1066 m	1520 s
(II)	<i>m</i> -Chloro phenylazo-bis-acetoxime	3195 m	1070 m	1512 s
(III)	<i>o</i> -Methyl phenylazo-bis-acetoxime	3260 m	1078 m	1520 s
(IV)	<i>m</i> -Methyl phenylazo-bis-acetoxime	3204 m	1068 m	1518 m
(V)	<i>p</i> -Bromo phenylazo-bis-acetoxime	3200 s	1070 m	1510 m
(VI)	<i>o</i> -Carboxyl phenylazo-bis-acetoxime	3350 m	1062 m	1514 s
(VII)	<i>p</i> -Sulphonamido phenylazo-bis-acetoxime	3250 w	1102 m	1515 m

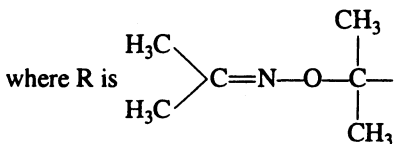
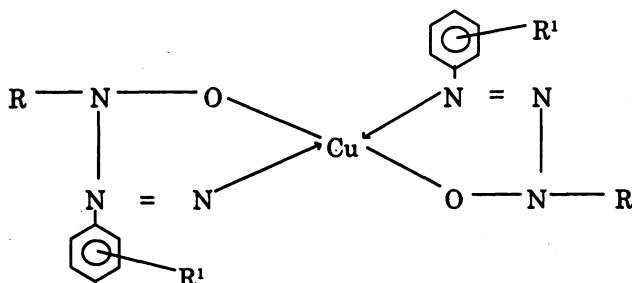
Complex formation is further supported by the fact that in all the seven cases v(N—N) band assigned in the range 1215–1197 cm⁻¹ and v(C—N) assigned in the range 1225–1218 cm⁻¹ either got submerged into one band or shifted to higher value indicating delocalisation of electrons resulting in strengthening of (N—N—) and (C—N) bonds. This delocalisation is possible due to complex formation. Thus this also supported complex formation with all the seven AABAs.

Similarly v(N → O) band assigned at 948 ± 6 cm⁻¹ in AABAs has been found to be shifted to higher values in all the seven complexes. This also supported strengthening of N → O bond due to complex formation.

Characteristic asymmetric band for >C=O of —COOH group is generally found in the range 1700–1660 cm⁻¹. In the present study this band appeared at

1667 cm^{-1} in case of compound VI. If the carbonyl group of $-\text{COOH}$ in compound VI taken part in complex formation this band would have shifted to much lower value. However in present case no such lowering of value of this band has been observed. Thus it can be concluded that $-\text{COOH}$ group of the compound VI was not involved in complex formation. It is perhaps due to steric hindrance which prevents carbonyl group of $-\text{COOH}$ to take part in bond formation with Cu(II) .

Thus it can be concluded that AABAs form square-planar complexes with copper(II) and their structure can be tentatively proposed as follows:



and R^1 may be $-\text{H}$, $-\text{Cl}$, $-\text{Br}$, $-\text{CH}_3$, $-\text{COOH}$, $-\text{SO}_2\text{NH}_2$ at *o*-, *m*- or *p*-position.

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