Research Article

Studies on the Formation and Composition of Copper(II)-α- and γ-Halo-1-Oxobutanilides Complexes

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Abstract The formation, structure, and relative stabilities of copper(II) complexes with γ-bromo-, p-tolyl-γ-bromo-, γ-iodo-, α-bromo-, α-chloro-, and α-phenyl-azo-γ-bromoacetoacetanilide (L) are investigated. The ultraviolet spectrophotometric study indicates the formation of the stable complex species $Cu(L)_{1-3}$ in solution. The formation constants of these complexes were computed from the spectrophotometric data. The solid complexes were prepared and chemically analyzed and their FT-IR spectra were studied. The structural formulae of the prepared chelates were proposed.

Keywords structure; relative stability; oxobutanilides; copper complexes, absorbing species

1. Introduction

Copper(II) complexes and other metal cations with acetoacetanilide and some of its derivatives have been studied by a group of investigators using different experimental techniques [1,2,3,4]. Zayed et al. [5] studied structures of 2-thiohydantoin and its metal chelates. Also, Zayed et al. [6] determined the stability constants of uranyl complexes potentiometrically. The effect of substituents on the phenyl ring and on the stability of these complexes was interpreted in terms of inductive, mesomeric, and sterric effects. CuL_2 complexes (HL = acetoacetanilide, o-chloroacetoacetanilide, and o-acctoacetacetatoludide) were prepared, their spectra were studied, and their stability constants were determined [7,8]. The stability constants of 13 oximes of acetoacetanilide and Cu^{2+}, UO_2^{2+}, and Be^{2+} complexes were determined by Kettrup [9] using potentiometric pH-measurements.

The wide applications and great importance of complexes of acetoacetanilide and its derivatives with copper directed our attention toward further studies on their structures, which was the aim of the present investigation. Acetoacetanilide complex can be used as fungicides and has a great influence in nitrification of soil. The complexes of these compounds with cations, especially those of Cr^{3+} and Cu^{2+}, are used for water proofing, tanning, and coloring and as parasiticides [10].

2. Experimental

2.1. Materials and methods

All chemicals used were of the highest purity available. They included γ-bromoacetoacetanilide (γ-Br-A.A.A.), p-tolyl-γ-bromoacetoacetanilide (p-tolyl-γ-Br-A.A.A.), γ-iodoacetanilide (γ-I-A.A.A.), α-bromoacetoacetanilide (α-Br-A.A.A.), α-chloroacetanilide (α-Cl-A.A.A.), and α-phenyl-azo-γ-bromoacetoacetanilide (α-C_6H_5-azo-γ-Br-A.A.A.) [11].

2.1.1. Preparation of complexes and their analysis

The solid complexes of copper acetate with γ- and α-haloacetoacetanilide were prepared by adding the calculated amount of ligand (dissolved in the least amount of ethanol) dropwise to 0.2–0.5 g copper acetate (dissolved in the least amount of water) with constant stirring. The solid complexes were spontaneously precipitated and separated from solution by filtration, washed with alcohol-water mixture, and left to dry in a vacuum desiccator for few days. These complexes were recrystallized from ethyl alcohol or acetone.

The molecular weights of these complexes were calculated from EDTA titration data [12]. Microanalyses of precipitated complexes for C, H, N, halogen, and metal were performed using the recommended procedures. The results are shown in Table 1.

2.1.2. Spectrophotometric studies

(I) Ultraviolet spectral measurements

The spectra of copper acetate and copper complexes with γ- and α-halo derivatives were scanned in 210–360 nm using a Beckmann DK-L recording spectrophotometer. The formation and composition of different copper complexes in solution were studied by applying Job's continuous variation method in the case of α-Br-A.A.A. and the molar ratio method (mrm) in the case of all ligands used [12].

Table 1: Analysis of copper(II) acetoactanilide complexes.

Ligand (L)	Color of the complex	Melting point		C%		H%		N%		Other elements		M. Wt.		Proposed formula of the complex M:L
		pure	mixed	Calc.	found	Calc.	found	Calc.	found	Calc.	found	Calc.	found	
		C*	C*							Cu%				
γ-Br-A.A.A.	Green	164	146	41.5	42.0	3.70	3.0	4.03	4.6	9.15	8.9	693.76	694.06	
													694.85	(CuL$_2$)(ACo)$_2$
		166	144		41.5		3.0		4.4				*701.00	
										Br%				
	Faint green	135	130	42.8	42.1	3.7	3.4	4.42	4.3	25.2	26.2	949.88	950.22	(CuL$_3$)(ACo)$_2$
		136	132		42.6		3.2		4.4				945.78	
p-totyl-γ-Br-A.A.A.	Pale green	163	150	43.7	43.8	4.15	4.4	4.6	4.5	26.5	27.5	603.33	605.01	
		162	151		44.3		3.9		4.6		27.4		*612.00	
3-phenyl-azo-γ-Br-A.A.A.	Chocolate brown	149	146	44.2	44.8	3.5	4.2	7.7	7.7	14.7	16.6	637.40	630.00	(CuL)(ACo)$_2$
							4.6		7.4				637.30	
	Brown	152	146	49.5	50.1	3.7	3.5	9.2	8.8	18.8	20.1	901.72	903.80	(CuL$_2$)(ACo)$_2$
		150			50.4		3.4		9.0				903.90	
										Cu%				
α-Br-A.A.A.	Pale green	164	148	41.5	41.0	4.6	4.2	40.2	4.8	9.15	9.13	693.76	693.33	(CuL$_2$)(ACo)$_2$
					41.2		4.1		4.4					
γ-I-A.A.A.	Bright green	152	139	37.1	36.6	3.3	2.6	4.7	4.6	8.1	8.09	787.32	787.89	(CuL$_2$)(ACo)$_2$
													792.45	
		153	138		36.3		3.1		4.3				790.00	
α-Cl-A.A.A.	Green	196	134	47.6	48.6	4.3	4.2	4.62	4.2	10.53	10.12	604.90	600.90	(CuL$_2$)(ACo)$_2$
		195	135		48.0		4.3		4.5				603.80	

*Molecular weights determined in the microanalytical unit.

(II) Infrared spectral measurements

The FT-IR spectra of the pure ligand and solid complexes were obtained by applying the KBr disc technique and using Pye Unicam SP1000 spectrophotometer.

3. Results and discussion

3.1. UV spectra

The spectra of copper acetate, ligands, and complex were scanned in the wavelength range of 210–360 nm. Representative curves for the data obtained by Job's method for Cu-γ-Br-A.A.A. complexes are shown in Figure 1.

The results obtained in this case are represented by the plot of absorbance against wavelength exhibiting maxima for various metals to ligand ratios, which may be attributed to the presence of more than one complex species. The presence of the most stable ML$_2$ complex is confirmed by the plot of absorbance against mL reagent at 300 and 330 nm. The data obtained in the case of other ligands by applying the mrm indicate the formation of the most stable 1:2 (M:L) complexes, except in the case of 3-C$_6$H$_5$-azo-γ-Br-A.A.A. where the results revealed the formation of 1:1 and 1:2 (M:L) adducts using the previously published technique of oxygen flask combustion [13].

3.2. Determination of the number of absorbing species

In order to determine the number of absorbing species in the cases of Cu(II) complexes with the above-mentioned ligands, Coleman graphical method is applied to the data obtained by applying the mrm (Tables 2–4). By plotting the variables $x = A_{ij} - A_{i'j'}$ against $y = A_{ij} - A_{i'j'}$, where i and j are two wavelengths and i' and j' are the corresponding concentrations of the investigated solutions,
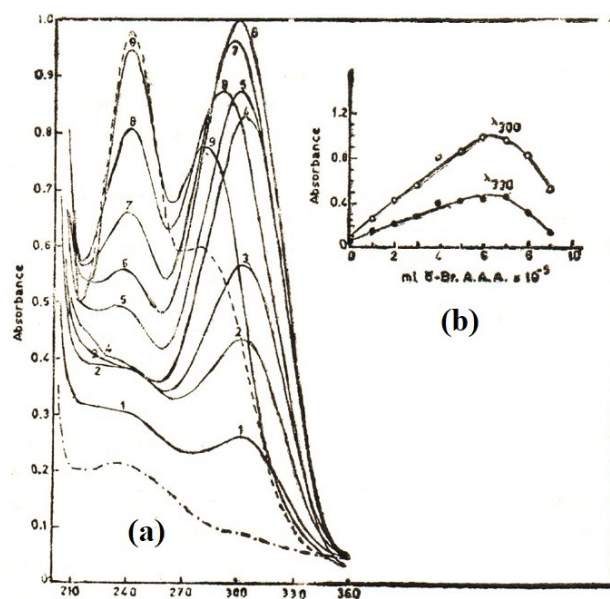

Figure 1: The ultraviolet absorption spectra of copper acetate. (a) γ-Br-A.A.A., and their complexes formed by the continuous variation method. (b) (Cu): 8×10^{-5} M, Br-A.A.A.: 9×10^{-5} M, and complexes of copper: ligand in ratios (1 = 9:1, 2 = 8:2, 3 = 7:3, 4 = 6:4, 5 = 5:5, 6 = 4:6, 7 = 3:7, 8 = 2:8, and 9 = 1:9).

straight lines were obtained, passing by the origin, in the cases of Cu-γ-Br-, p-tolyl-γ-Br-, γ-iodo-, α-Br-, and α-Cl-A.A.A., indicating the presence of two absorbing species in solution, namely, the ligand and the stable 1:2 (M:L) complex. Figure 2 is a representative of this. These are interpreted depending upon previously published work by Zayed et al. [14, 15, 16, 17, 18].

Table 2: Absorption matrices for the copper complex with acetoacetanilide derivatives in the UV range. (a) Cu-γ-Br-A.A.A., (b) Cu-p-tolyl-γ-Br-A.A.A., (c) Cu-α-phenyl-azo-γ-Br-A.A.A., and (d) Cu-γ-I-A.A.A.

		\[γ-Br-A.A.A.\] $\times 10^{-5}$ M							
Wavelength		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
		(Soln. no., j)							
i	nm	1	2	3	4	5	6	7	8
1	300	0.175	0.260	0.312	0.405	0.480	0.550	0.595	0.680
2	306	0.178	0.253	0.297	0.380	0.412	0.500	0.525	0.620
3	294	0.165	0.255	0.419	0.411	0.490	0.580	0.632	0.723
4	240	0.151	0.270	0.370	0.475	0.597	0.755	0.865	1.000
5	228	0.140	0.240	0.303	0.387	0.480	0.600	0.670	0.770

(a)

		\[p-tolyl-γ-Br-A.A.A.\] $\times 10^{-5}$ M							
Wavelength		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
		(Soln. no., j)							
i	nm	1	2	3	4	5	6	7	8
1	306	0.200	0.295	0.340	0.375	0.503	0.600	0.578	0.640
2	294	0.192	0.292	0.292	0.422	0.542	0.668	0.692	0.741
3	288	0.180	0.280	0.350	0.431	0.542	0.668	0.690	0.768
4	270	0.148	0.232	0.312	0.416	0.498	0.610	0.650	0.710
5	240	0.199	0.324	0.454	0.625	0.735	0.935	1.020	1.165

(b)

		\[3-phenyl-azo-γ-Br-A.A.A.\] $\times 10^{-5}$ M					
Wavelength		0.5	1.0	2.0	3.0	4.0	5.0
		(Soln. no., j)					
i	nm	1	2	3	4	5	6
1	240	0.105	0.170	0.364	0.480	0.595	7.15
2	270	0.075	0.135	0.205	0.380	0.470	0.545
3	276	0.080	0.140	0.310	0.410	0.505	0.600

(c)

		\[γ-I-A.A.A.\] $\times 10^{-5}$ M							
Wavelength		0.5	1.0	1.5	1.75	2.0	3.0	3.5	4.0
		(Soln. no., j)							
i	nm	1	2	3	4	5	6	7	8
1	228	0.130	0.235	0.360	0.385	0.460	0.620	0.710	0.730
2	240	0.120	0.237	0.380	0.410	0.510	0.710	0.755	0.813
3	252	0.088	0.190	0.320	0.335	0.410	0.590	0.625	0.645
4	270	0.075	0.148	0.230	0.250	0.290	0.395	0.435	0.395
5	300	0.135	0.250	0.360	0.415	0.470	0.580	0.640	0.670
6	310	0.160	0.300	0.415	0.460	0.520	0.620	0.680	0.710

(d)

Table 3: Absorption matrices for the copper complexes with acetoacetanilide derivatives in the UV range. Cu-α-Br-A.A.A.

|		\[α-Br-A.A.A.\] $\times 10^{-5}$ M									
Wavelength		0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0	4.0
		(Soln. no., j)									
i	nm	1	2	3	4	5	6	7	8	9	10
1	288	0.052	0.058	0.090	0.105	0.130	0.150	0.185	0.230	0.270	0.290
2	252	0.108	0.152	0.203	0.252	0.295	0.355	0.445	0.540	0.640	0.690
3	246	0.104	0.148	0.195	0.235	0.275	0.335	0.410	0.505	0.625	0.695
4	240	0.108	0.138	0.158	0.215	0.245	0.293	0.360	0.422	0.501	0.535
5	228	0.115	0.140	0.195	0.218	0.265	0.300	0.345	0.392	0.400	0.415
6	288	0.052	0.058	0.090	0.105	0.130	0.150	0.185	0.230	0.270	0.290
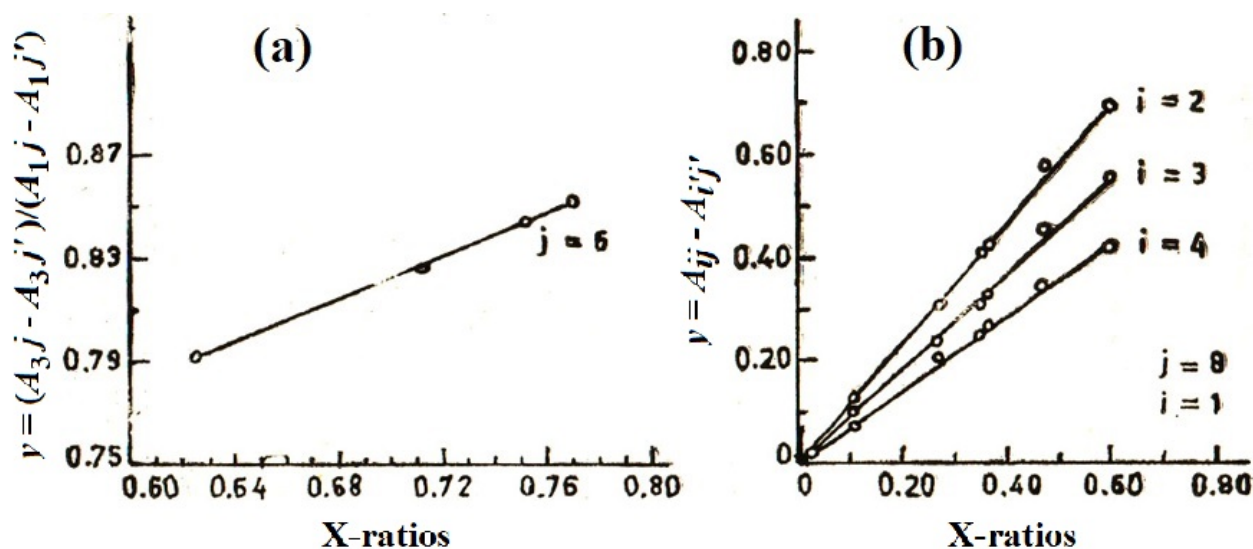
Figure 2: Number of absorbing species in solution from spectrophotometric data in the UV range: (a) Cu-α-phenyl-azo-γ-Br-A.A.A. absorbing species; (b) Cu-γ-I-A.A.A. absorbing species.

Table 4: The calculated conventional formation constants of complexes.

Ligand	$\log K$ of 1:2 (M:L) complexes
γ-I-A.A.A.	10.50
α-Br-A.A.A.	11.13
γ-Br-A.A.A.	11.28
α-Cl-A.A.A.	11.77
3-C_6H_5-azo-γ-Br-A.A.A.	11.95
p-C_7H_7-γ-Br-A.A.A.	12.65

On the other hand, by plotting,

$$x = (A_2j - A_2j')/(A_1j - A_1j').$$

In the case of 3-C_6H_5-azo-γ-Br-A.A.A., a straight line is obtained revealing the existence of three absorbing species (Table 1), namely, the organic ligand and the 1:1 and 1:2 (M:L) complexes. All these complex species have been isolated in the solid state and their compositions are confirmed by chemical analysis and FT-IR spectra.

These data are interpreted depending upon the previously published data by Zayed et al. [18, 19, 20, 21] and used to prove the proposed structures of studied complexes.

3.3. Determination of the stability constants

The calculated conventional formation constants using the recommended method $\log K$ of 1:2 (M:L) are tabulated in Table 4.

These values indicate higher stabilities than those of copper-phenyl substituted acetoacetanilide (6.4–7.27 g in 50% dioxane, 8.08–9.3 g in 75% dioxane, and 5.45–10.57 g in 30–60% dioxane 1 for all possible N-substituted

anilides 2, obtained from potentiometric-pH measurements). They also indicate that stability increases in cases where there are substituents in the α-position and phenyl ring simultaneously as in the case of p-tolyl-γ-Br-A.A.A. ($\log K = 12.65$). The lower $\log K$ values obtained by potentiometric methods may be interpreted on the basis that in potentiometry, the acidity, equivalent to the protons liberated when the metal ion is chelated with the enol form of the regent, is measured. However, since a great portion of the reagent is present in the ketoform, it is clear that the latter will contribute to the stability of the complex.

3.4. Infrared absorption spectra (FT-IR)

The FT-IR spectra of all separated solid complexes were studied. In the case of the Cu-γ-Br-A.A.A. complex, as a representative example, its spectrum (Figure 3) showed intensified broad band at $1,730\,\text{cm}^{-1}$ and anilide carbonyl band at $1,660\,\text{cm}^{-1}$. Comparing the FT-IR bands of the complex with that of the γ-Br-A.A.A., it is clear that the two carbonyls are linked via coordinate bonds to Cu(II) ions. The more intensified NH band at $3,300\,\text{cm}^{-1}$ in the 1:2 complexes than that in the ligand supports the presence of two moles of the ligand in the complex [14, 15, 16, 17]. The halogen carbon peaks in both ligands and metal chelates skeletons are intensively present in wave numbers 625–$800\,\text{cm}^{-1}$; their positions are varied in ligands due to the variation of halogen kind and also in chelates as a result of complex nature and stability.

The general formula of the given complexes depending on the FT-IR studies may tentatively be represented by the equilibrium of both keto and enol forms (I and II) of the ligand attached to copper ions as given in Figure 4.
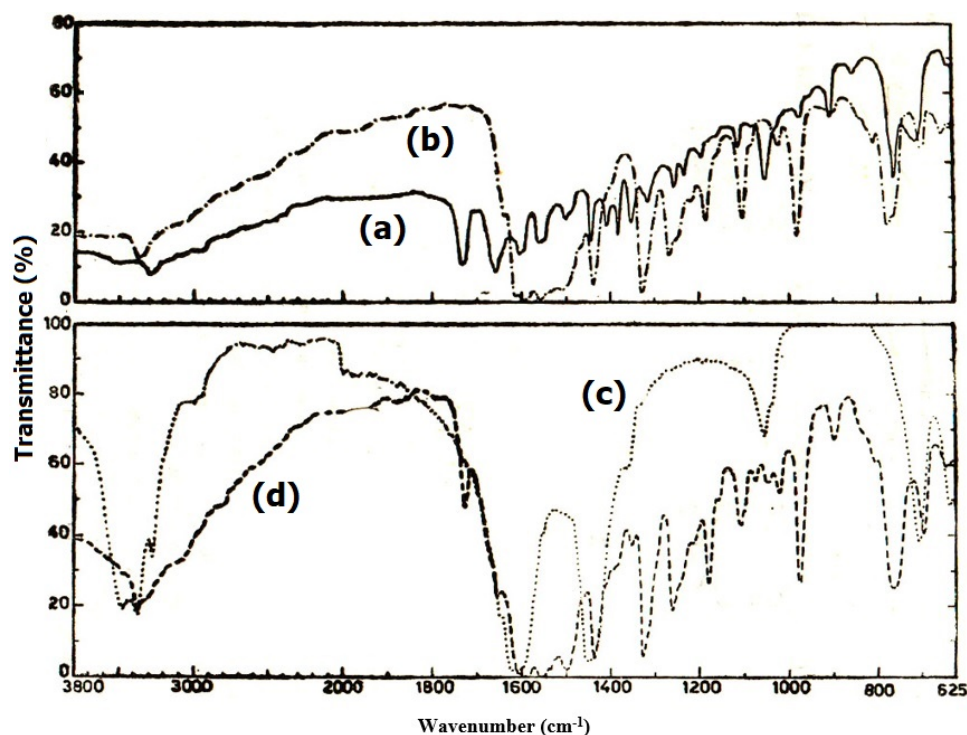
Figure 3: The infrared spectra of γ-Br-A.A.A. and its complexes with copper acetate. (a) γ-Br-A.A.A., (b) Cu-Br-A.A.A. (1:3), (c) copper acetate, and (d) Cu-γ-Br-A.A.A. (1:2).
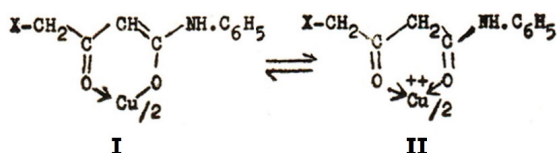

Figure 4: The proposed equilibrium between keto-enol structures of γ-Br-A.A.A. copper complexes.

Conflict of interest The author declares that he has no conflict of interest.

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