Structural Studies of Cu(II) Chelates with Some Arylidene Derivatives of Benzilic Hydrazide

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Summary. The Cu(II) chelates of some new arylidene derivatives of benzilic hydrazide have been synthesized and were characterized by elemental and thermal analyses, as well as by IR, UV/Vis, ESR, and X-ray spectroscopy. The data revealed the formation of tetrahedral 1:1 (L:M) and square planar 2:1 and 1:2 complexes. In the 1:1 complexes, the organic compounds behave as dibasic tridentate ligands towards the Cu(II) ion, whereas in the 1:2 or 2:1 complexes they behave as monobasic bidentate substituents.

**Keywords.** Copper chelates; Hydrazones; Benzilic hydrazides.

**Strukturuntersuchungen an Chelaten von Cu(II) mit einigen Arylidenderivaten
des Benzilsäurehydrazids**

Zusammenfassung. Die Cu(II)-Chelate einiger neuer Arylidenderivate des Benzilsäurehydrazids wurden synthetisiert und mittels Elementaranalyse, Thermogravimetrie und Differentialthermoanalyse sowie IR-, UV/Vis-, ESR- und Röntgenspektroskopie untersucht. Die erhaltenen Daten zeigen, daß tetraedrische 1:1- und quadratisch-planare 2:1- und 1:2-Komplexe gebildet werden. In den 1:1-Komplexen verhalten sich die organischen Verbindungen wie dibasische dreizähnige Liganden, während sie in den 1:2- und 2:1-Komplexen in monobasischer zweizähniger Form vorliegen.

Introduction

Arylidene acid hydrazides are known to act as chelating agents [1–4]. The interest in the study of these compounds and their metal chelates arose from their behaviour as efficient antituberculous remedies based on the tendency to form metal chelates with transition metal ions [5–7]. The reaction of arylidene acid hydrazides with transition metal ions proceeds according to one of the following paths depending on the nature of metal ion, the anion of its salt, and the alkalinity of the medium used [8–11].

Some aroylhydrazones have been used as analytical reagents for the colorimetric and fluorimetric determination of some metal ions [12, 13]. Metal chelates with some hydroxy phenylhydrazones have been prepared and investigated [14, 15] which have shown that the presence of an OH group in *o*-position
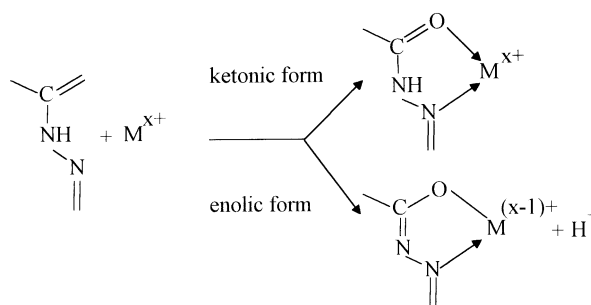
Scheme 1

influences markedly the behaviour of the ligand. The composition of metal complexes with 1-phenyl-3-methyl-4-naphthonyl-5-pyrazolone in alcoholic solutions has been studied spectrophotometrically [16].

The present investigation deals with the preparation of Cu(II) complexes with some new arylidene derivatives of benzilic hydrazide using Cu(II) acetate as salt. The chelates obtained were characterized by elemental analysis, TG, DTA, IR, UV/ Vis, ESR and X-ray spectroscopy.

Results and Discussion

The results of elemental analyses of the solid Cu(II)-benzilic hydrazone complexes are recorded in Table 1 and are in good agreement with the suggested molecular formulae. All complexes are associated with coordinated water or ethanol molecules which are not removed by applying vacuum for 2–3 h at room temperature. From the analysis data it can be concluded that ligands I_g, I_i, and I_k form 1:1 and 1:2 ($Cu^{2+}:L$) complexes, whereas ligands I_c, I_d, I_e, I_f, I_h, and I_j form only 1:1 complexes. A binuclear complex of the formula ($Cu_2I_a(AcO)_2 \cdot H_2O$) is formed with the ligand I_a. Ligand I_b forms a 1:2 complex only.

The aim of the thermal analysis study is to obtain information concerning the thermal stability of the investigated chelates, to decide whether the water or ethanol molecules are inside or outside the coordination sphere, and to suggest a general scheme for the thermal decomposition of these chelates [17, 18].

The thermograms of ($Cu(I_a)(AcO)_2 \cdot (H_2O)$), $Cu(I_b)_2(EtOH)_2$), and ($Cu(I_g)_2 \cdot$ EtOH), ($Cu(I_i) \cdot (EtOH)H_2O$) are shown in Fig. 1. The upper part of the thermogram shows the removal of ethyl alcohol molecules from the complex under investigation at 50–290°C. The anhydrous or unsolvated complex is thermally stable up to 270–335°C. In case of ($Cu(I_a)(AcO)_2 \cdot (H_2O)$), the removal of acetate anions is achieved at 225–275°C. The decomposition of the complex to Cu_2O starts within the temperature range of 250–370°C. The DTA curves of the investigated chelates show exothermic peaks at 70°C which are due to the removal of humidity, *i.e.* physically adsorbed water molecules from the outer surface of the crystal lattice. On the other hand, the exothermic peaks within the range of 140–235°C are due to the removal of coordinated water and/or ethyl alcohol molecules. At higher temperatures, some lattice rearrangements at the beginning of the melting of the anhydrous complex, followed by a phase transformation accompanying
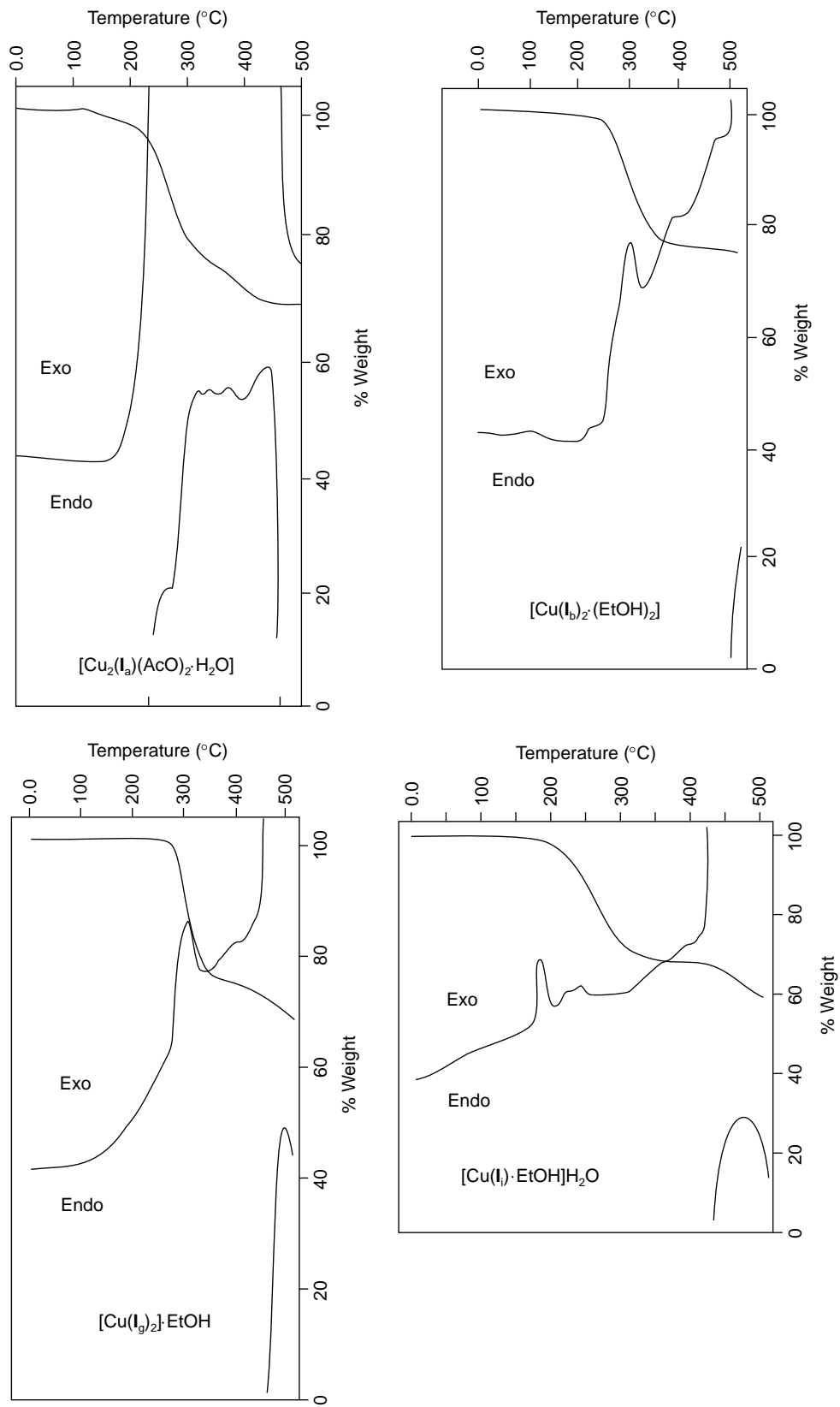
Fig. 1. TG-DTA curves of some benzilic hydrazone-Cu^{II} complexes

Table 1. Analytical and EPR data of Cu(II)-benzilic hydrazone complexes

Complex	M:L	Colour	%C Found	%C Calc.	%H Found	%H Calc.	%N Found	%N Calc.	%Cu(II) Found	%Cu(II) Calc.	EPR values $g_z = g_{/\!/}$	$g_x = g_\perp$	g_y	g_{iso}
$[Cu_2(\mathbf{I_a})(AcO)_2 \cdot H_2O]$	2:1	greenish brown	50.17	49.87	3.82	3.95	4.54	4.61	21.02	20.92	2.093	2.009	2.045	2.049
$[Cu(\mathbf{I_b})_2 \cdot (EtOH)_2]$	1:2	brown	62.32	62.55	4.92	4.99	6.76	6.35	7.59	7.20				
$[Cu(\mathbf{I_c}) \cdot H_2O]$	1:1	yellowish brown	56.41	56.76	4.39	3.83	6.13	6.31	14.49	14.30				
$[Cu(\mathbf{I_d}) \cdot EtOH] H_2O$	1:1	brown	51.83	51.63	4.11	4.30	4.99	5.28	12.04	11.88				
$[Cu(\mathbf{I_e}) \cdot EtOH] EtOH$	1:1	greenish brown	56.45	56.76	5.14	5.11	8.83	7.95	12.70	12.02				
$[Cu(\mathbf{I_f}) \cdot H_2O] H_2O$	1:1	brown	53.08	53.33	4.09	4.02	8.22	8.89	13.48	13.44				
$[Cu(\mathbf{I_g}) \cdot EtOH]$	1:1	dark green	62.48	62.43	5.38	5.41	9.30	8.74	12.93	13.22	–	–	–	2.006
$[Cu(\mathbf{I_g})_2 \cdot EtOH]$	1:2	dark green	67.52	67.49	5.69	5.86	9.81	9.84	7.80	7.44				
$[Cu(\mathbf{I_h}) \cdot H_2O]$	1:1	yellowish green	60.28	60.07	3.96	4.55	6.57	6.37	14.39	14.45				
$[Cu(\mathbf{I_i}) \cdot EtOH] H_2O$	1:1	brownish yellow	58.96	59.32	4.89	5.36	6.50	5.77	13.06	13.08				
$[Cu(\mathbf{I_i})_2]$	1:2	brownish yellow	66.49	66.71	5.98	5.32	7.35	6.77	7.45	7.67				
$[Cu(\mathbf{I_j}) \cdot H_2O] \cdot 2H_2O$	1:1	yellowish brown	61.94	61.64	5.03	5.36	6.70	6.25	6.88	7.09	–	–	–	2.004
$[Cu(\mathbf{I_k}) \cdot H_2O]$	1:1	light brown	62.32	62.34	4.19	4.72	6.85	6.61	15.38	14.99				
$[Cu(\mathbf{I_k})_2] \cdot 3H_2O$	1:2	light brown	65.95	65.71	5.71	5.48	7.30	6.97	8.18	7.90	–	–	–	2.003

Table 2. TG-DTA of some Cu(II)-benzilic hydrazone complexes

Complex	Temperature (°C)		TG	DTA		% Loss		Assignment
	Decomp. Init.	Temp. Cu-lig core	Thermal step	Exo	Endo	Found	Calc.	
$[Cu_2(I_a)(AcO)_2 \cdot H_2O]$	50	280	50–140	140	–	3.10	2.97	Coordinated H_2O
$[Cu_2(I_a) \cdot (AcO)_2]$			140–225	225	–	12.90	12.69	One acetate ion
$[Cu_2(I_a) \cdot AcO]$			225–275	275	–	22.41	22.61	One acetate ion
$[Cu_2(I_a)]$			275–280	–	–	–	–	Thermal stability
			280	325	–	–	–	Decomposition and formation of Cu_2O
$[Cu(I_b)_2(EtOH)_2]$	50	335	50–270	195	–	5.00	5.21	Coordinated EtOH
$[Cu(I_b)_2 \cdot EtOH]$			270–290	235	–	10.55	10.42	Coordinated EtOH
$[Cu(I_b)_2]$			290–335	–	–	–	–	Thermal stability
$[Cu(I_b)]^+$			335–370	350	–	51.66	51.62	One molecule of ligand
			370	–	–	–	–	Decomposition and formation of Cu_2O
$[Cu(I_g)_2] \cdot EtOH$	50	290	50–70	70	–	5.00	5.39	Lattice EtOH
$[Cu(I_g)_2]$			70–290	–	–	–	–	Thermal stability
$[Cu(I_g)]^+$			290–315	300	–	48.88	48.97	One molecule of ligand
			315	–	–	–	–	Decomposition and formation of Cu_2O
$[Cu(I_j) \cdot EtOH] \cdot H_2O$	50	250	50–70	70	–	3.50	3.70	Lattice H_2O
$[Cu(I_j) \cdot EtOH]$			70–175	175	–	13.04	13.18	Coordinate EtOH
$[Cu(I_j)]$			175–250	–	–	–	–	Thermal stability
			250	–	–	–	–	Decomposition and formation of Cu_2O

the oxidation of the organic ligands, are observed. Finally, the thermal decomposition leads to the formation of Cu_2O. The percentage losses in weight of the complexes, calculated from the TG curves, are given in Table 2. Obviously $(Cu(I_b)_2(EtOH)_2)$ has the highest thermal stability among the complexes under investigation. The thermal stability increases in the order $(Cu(I_b)_2(EtOH)_2) > Cu(I_g)_2)EtOH > (Cu(I_a)(AcO)_2 \cdot H_2O) > (Cu(I_i)EtOH)$. This runs parallel with the substituent effect of the hydrazone ligands according to m-Cl $(I_b) > p$-$N(CH_3)_2$ $(I_g) > p$-OH $(I_a) > p$-OCH_3 (I_i).

The IR spectra of all complexes (see Table 3) exhibit a broad band around 3500–$3415 \, cm^{-1}$ which is attributed to ν(OH) of water and/or EtOH molecules associated with the central Cu(II) ion in the complex. All 1:1 complexes have the same general IR spectroscopic features. ν(OH)-alcoholic and ν(OH)-enolic disappear in the spectra of free ligands when the ligands reacted with Cu(II). The bands corresponding to δ(OH) and γ(OH) in the spectra of free benzilic hydrazones are absent in the spectra of the Cu(II) complexes. This can be ascribed to the displacement of two protons, probably from the alcoholic and enolic OH groups of the free hydrazones, by the Cu(II) ion leading to a covalent linkage with these ligands. Also, the ν(C=N) band is splitted into two different bands at 1615–$1585 \, cm^{-1}$ and 1650–$1620 \, cm^{-1}$ due to free and coordinated C=N groups, respectively. A support of the above idea is the appearance of nonligand bands (ν(M–O) and ν(M–N) at 517–$405 \, cm^{-1}$ and 420–$328 \, cm^{-1}$, respectively). In case of the 1:2 complexes, ν(OH)-enolic of the free ligands cannot be observed in the spectra of Cu(II) complexes, whereas the ν(OH) band of the alcoholic group in the free hydrazones can still be observed at the same position. A support of this behaviour is gained from the obvious decrease in the intensity of δ(OH) at 1359–$1320 \, cm^{-1}$ and ν(C-OH) at 1059–$1054 \, cm^{-1}$ in the spectra of the Cu(II) complexes; the remaining bands are due to the alcoholic group. The ν(C=N) band is splitted into two different bands located at 1660–$1640 \, cm^{-1}$ in the spectra of the Cu(II) complexes, corresponding to free and coordinated C=N groups, respectively. As above, nonligand bands appear at 530–425 and 420–$337 \, cm^{-1}$ due to ν(M–O) and ν(M–N), respectively.

In case of the binuclear 2:1 complex with ligand I_a, ν(OH)-phenolic and ν(OH)-enolic bands located at 3200 and $3060 \, cm^{-1}$, respectively, disappear when the ligand reacts with Cu(II) ion, whereas, ν(OH)-alcoholic is still present at the same position ($3330 \, cm^{-1}$) as in the spectrum of the free ligand. The δ(OH) and γ(OH) bands in the spectra of the free hydrazones are still observed at the same position as in the spectrum of Cu(II) complex, but with lower intensity. The appearance of C=N bands at two different wavenumbers (1640 and $1581 \, cm^{-1}$) in the spectrum of the Cu(II) complex is due to coordination of one azomethine nitrogen; hence, the bands can be assigned to the free and coordinated C=N groups, respectively. New bands appear in the spectrum of the Cu(II) complex which are not present in the spectrum of free hydrazone ligand, located at 1510, 1443, 506, and $533 \, cm^{-1}$ due to ν(COO_{as}), ν(COO_s), ν(M–O), and ν(M–N), respectively. The first two bands indicate the coordinated nature of the acetate as a bridging bidentate ligand.

In coordination compounds, spectroscopic interactions can be classified as ligand spectra ($L \rightarrow L$), charge transfer (CT) spectra from the metal to the ligand

Table 3. IR and visible bands of Cu(II)-benzilic hydrazone complexes

Complex	Ratio	ν(OH) H₂O/EtOH	ν(OH) alc.	ν(C=N) free	ν(C=N) coord.	δ(OH)	γ(C-OH)	ν(M-O)	ν(M-N)	Visible (λ, nm) DMF	Nujol
[Cu(I$_c$)·H$_2$O]	1:1	3481	–	1645 sh	1590	–	–	405	330	800, 600	840, 590
[Cu(I$_d$)·EtOH]	1:1	3441	–	1625	1585 sh	–	–	427	342	800, 605	850, 620
[Cu(I$_e$)·EtOH]·EtOH	1:1	3415	–	1645	1610 sh	–	–	425	330	800, 650	860, 640
[Cu(I$_f$)·H$_2$O]·H$_2$O	1:1	3474	–	1645 sh	1615 sh	–	–	420	328	–	855, 650
[Cu(I$_g$)·EtOH]	1:1	3432	–	1645 sh	1615	–	–	517	420	800, 600	860, 600
[Cu(I$_h$)·H$_2$O]	1:1	3434	–	1650 sh	1597	–	–	491	329	800, 620	870, 660
[Cu(I$_i$)·EtOH]·H$_2$O	1:1	3500	–	1640 sh	1599	–	–	425	335	800, 600	860, 670
[Cu(I$_j$)·H$_2$O]·2H$_2$O	1:1	3467	–	1620	1585	–	–	427	376	800, 595	860, 660
[Cu(I$_k$)·H$_2$O]	1:1	3498	–	1640 sh	1600	–	–	424	339	800, 585	860, 560
[Cu(I$_b$)$_2$·(EtOH)$_2$]	1:2	3500	3339	1640	1595	1359	1056	443	408	790, 620	850, 650
[Cu(I$_g$)$_2$]·EtOH	1:2	3540	3431	1640	1586	1320	1059	485	419	800, 570	850, 590
[Cu(I$_i$)$_2$]·EtOH	1:2	3498	3400	1640 sh	1598	1322	1056	425	337	800, 600	840, 595
[Cu(I$_k$)$_2$]·3H$_2$O	1:2	3499	3340	1646	1600	1324	1054	476	339	785, 620	870, 560

Table 4. X-ray diffraction data of some benzilic hydrazones and some of their Cu(II) complexes

I_c		I_g		I_k		$[Cu(I_c) \cdot H_2O]$		$[Cu(I_g) \cdot EtOH]$		$[Cu(I_k) \cdot H_2O]$	
d (Å)	$I/I°$	d (Å)	$I/I°$	d (Å)	$I/I°$	d (Å)	$I/I°$	d (Å)	$I/I°$	d (Å)	$I/I°$
13.39	50	14.03	77	13.81	100	12.99	30	11.19	20	11.05	100
7.25	100	9.51	62	8.35	8	10.78	90	9.83	52	10.28	33
6.71	13	9.03	5	7.63	22	10.05	100	7.90	53	8.04	39
6.61	8	7.76	14	7.38	70	8.12	23	7.03	79	7.25	79
6.19	57	7.44	26	7.14	35	7.76	32	6.15	55	6.97	49
5.83	9	7.03	27	6.28	24	7.03	37	5.47	22	6.81	24
5.28	54	6.76	12	5.91	6	6.71	19	5.13	100	6.24	13
5.07	12	6.51	8	5.34	60	6.15	22	4.77	14	6.03	13
4.67	27	6.03	7	4.98	12	5.75	69	4.27	37	5.91	13
4.46	51	5.54	32	4.77	8	5.44	22	4.08	42	5.75	13
4.35	13	5.22	10	4.35	16	5.19	40	3.87	16	5.41	14
4.19	34	4.96	15	4.27	18	5.04	32	3.65	20	5.22	67
4.15	20	4.75	24	4.11	15	4.72	78	3.59	65	5.04	18
3.97	10	4.67	17	4.00	8	4.44	37	3.35	13	4.85	94
3.87	30	4.53	100	3.90	18	4.29	29	3.21	7	4.23	15
3.77	54	4.15	17	3.77	29	4.25	29	2.94	9	4.15	28
3.62	16	4.02	12	3.68	14	4.10	35	2.71	5	3.97	94
3.53	38	3.93	18	3.53	34	3.97	55	2.52	5	3.85	17
3.47	36	3.71	43	3.43	6	3.87	47	2.39	5	3.66	9
3.30	16	3.62	24	3.33	6	3.75	29	2.29	5	3.55	25
3.15	8	3.55	22	3.12	11	3.59	19	2.15	5	3.43	9
3.04	9	3.38	7	2.71	5	3.53	19	2.05	5	3.34	38
2.98	12	3.30	5	2.67	6	3.35	32	–	–	3.21	18
2.86	5	3.14	13	–	–	3.30	36	–	–	3.14	14
2.72	5	3.10	14	–	–	3.16	15	–	–	3.02	22
2.67	8	–	–	–	–	3.08	15	–	–	2.94	8
2.62	6	–	–	–	–	3.02	22	–	–	2.75	10
2.51	5	–	–	–	–	2.88	29	–	–	2.73	10
2.33	5	–	–	–	–	2.80	10	–	–	2.55	6
2.17	5	–	–	–	–	2.46	8	–	–	2.47	51
2.09	6	–	–	–	–	2.37	8	–	–	2.40	12

($M \rightarrow L$, metal oxidation) or from the ligand to the metal ($L \rightarrow M$, metal reduction), and ligand-field spectra within the d-orbitals of the metal that have been splitted in a ligand field (d $\rightarrow$ d transitions) [19–21]. The majority of the six coordinated Cu(II) complexes are tetragonally distorted, and their spectra exhibit one absorption band in the visible region above 650 nm whereas, the square planar structure shows a broad band at 625–700 nm. From the data given in Table 3 it can be seen that there are slight differences between the nujol mull spectra of the solid complexes and the spectra of the complexes in *DMF* solution. The electronic absorption spectra of the Cu(II) complexes under investigation show one or two broad bands with λ_{max} situated at 560–670 and 785–870 nm for benzilic hydrazone-Cu(II) complexes. The last two bands can be assigned to $^2B_{1g} \rightarrow {}^2B_{1g}$ and $^2E_g \rightarrow {}^2B_{1g}$ transitions, respectively.

The interplanar spacing and the relative X-ray intensities of the complexes $(Cu(I_c) \cdot H_2O)$, $(Cu(I_g) \cdot EtOH)$, and $(Cu(I_k \cdot H_2O)$ are given in Table 4. On comparing the X-ray diffraction patterns of each hydrazone with those of its corresponding Cu(II) complexes, the following can be pointed out:

i) The diffraction patterns of Cu(II) complexes are completely different in the interplanar distances and relative intensities from those of the corresponding ligand.

ii) The relatively high background and the broadening of the diffraction lines observed in the diffraction patterns of the Cu(II) complexes can be attributed to the small crystallite size and the strain occuring in the crystal lattice. This in turn can be ascribed to the possible orientation of the ligand molecules or the distortion of the coordination polyhedron around the Cu(II) ion [22]. The changes in *d* and I/I° in benzilic hydrazone Cu(II) complexes may be attributed to different structures, *i.e.* an involvement of a number of lattice or coordinated water/ethanol molecules, the different orientation of the ligands around the central Cu(II) ion [23], the various spherical rotations around the lattice axes, diffraction planes, and transition group operations [24].

Electon paramagnetic resonance (EPR) spectra of some Cu(II) complexes at room temperature show generally three, two, or one broad signals depending on the nature of the ligands used and the type of complex formed. The *g* values ($g_\perp$ and $g_{//}$) which reflect the geometry of the Cu(II) environment are given in Table 1. Generally, these compounds are not magnetically dilute; therefore, exchanges [25] and/or dipolar forces are expected to operate in which case the anisotropy is likely to be reduced. This appears to be the case for $(Cu(I_g)EtOH)$ and $(Cu(I_j) \cdot H_2O) \cdot 2H_2O$, and $(Cu(I_k)_2) \cdot 3H_2O$ complexes where only a single EPR line can be detected.

Based on the above results, the structure of the 1:1 (*M*:*L*) complexes formed between Cu(II) ion and the ligands under investigation can be represented as follows:
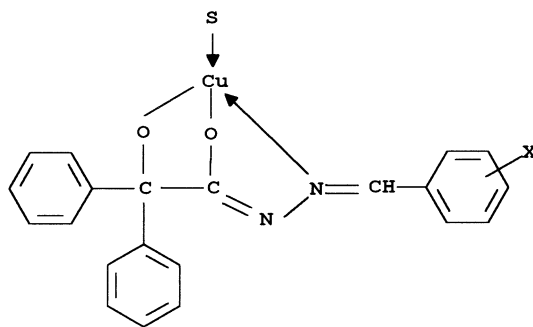
Scheme 2

Both 1:2 (*M*:*L*) complexes and $(Cu_2(I_a)(AcO)_2 \cdot H_2O)$ have a square planar structure.

The formulae obtained reveal that the hydrazones behave as dibasic tridentate ligands in case of 1:1 complexes and monobasic bidentate ones in 1:2 complexes. Ligand I_a behaves as a dibasic tridentate ligand towards the two copper ions. The coordinated nature of the acetate ions in the binuclear complex is supported by the
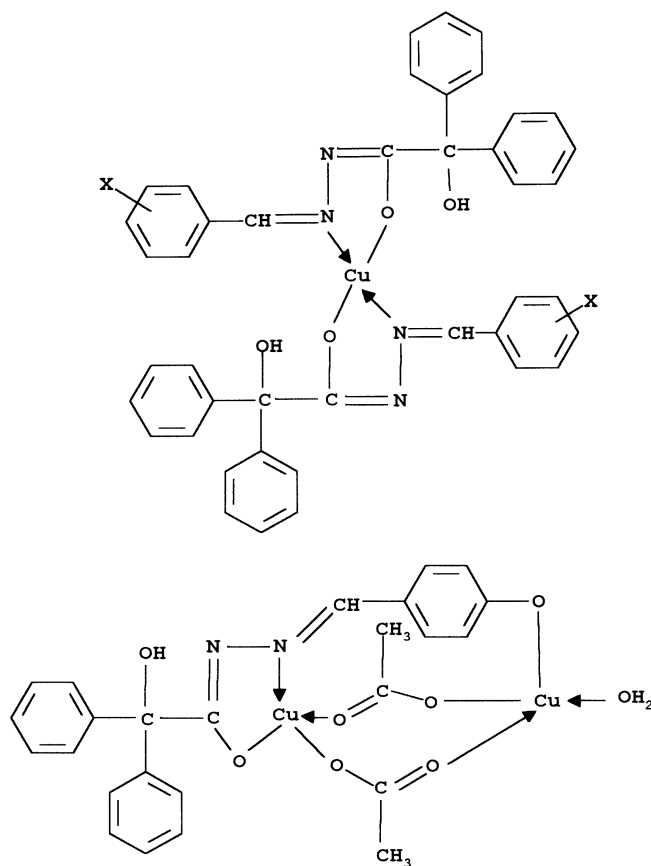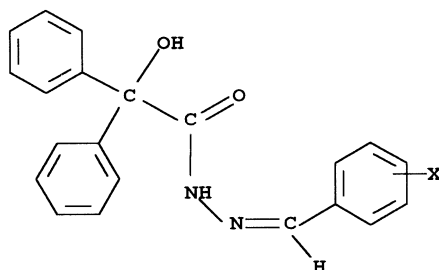
Scheme 3

fact that the addition of FeCl$_3$ solution to the complex solution gives a negative test for the acetate ion.

Experimental

All chemicals used in the present investigation were of B.D.H. grade.

The arylidene derivatives of benzilic hydrazide (0.01 mol in ethanol) with benzaldehyde derivatives (0.01 mol in ethanol). The reaction mixture was refluxed on a water bath for 1–4 h. The hydrazones separated on cooling and were filtered, recrystallized from ethanol, and dried in a desiccator over silica gel. The ligands used have the general formula

Scheme 4

where $X = p$-OH (a), m-Cl (b), p-Cl (c), m-Br (d), o-NO$_2$ (e), m-NO$_2$ (f), p-N(CH$_3$)$_2$ (g), o-CH$_3$ (h), p-OCH$_3$ (i), 3,4(OCH$_3$)$_2$ (j), and p-CH$_3$ (k).

The purity of the ligands was determined from the results of elemental analysis, IR, ^{1}H NMR, and UV/Vis spectra as described elsewhere [26].

The Cu(II)-hydrazone complexes were prepared by mixing the organic ligand solution (0.01 or 0.02 mol in ethanol) with 0.02 or 0.01 mol of Cu(II) acetate in ethanol. The mixture was refluxed for 6–24 h on a water bath. The solid complexes obtained were filtered, washed with ethanol, and dried in a desiccator over silica gel.

The thermogravimetric analysis of the Cu(II) complexes was carried out using a Netzsch Gerätebau Bestell Nr 348472 C thermal analyser. The weight loss was measured from ambient temperature up to 500°C in a rate of 5 degrees per minute.

The IR spectra were recorded using a Perkin Elmer 983 double beam infrared spectrophotometer (KBr disc) within the range of 4000–200 cm^{-1}. The visible spectra were recorded as nujol mulls and as saturated *DMF* solutions using a Perkin Elmer Lambda 5 spectrophotometer.

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