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Synthesis and Characterization of Cu(II) Complexes with New Mandelic Hydrazones

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SYNTHESIS AND CHARACTERIZATION OF Cu(II) COMPLEXES WITH NEW MANDELIC HYDRAZONES

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ABSTRACT

Cu(II) chelates of a series of new derivatives of mandelic hydrazones have been synthesized and characterized using elemental and TG analyses. IR, UV-Visible and EPR spectra. X-ray diffraction patterns were used to study their structure and geometry. The study revealed that Cu(II) complexes can exhibit square planar, tetrahedral or distorted octahedral structure depending on the nature of the ligands used and the stoichiometric ratio between the metal and ligand.

INTRODUCTION

Hydrazones¹ are compounds derived from the condensation of hydrazines with carbonyl compounds, namely aldehydes and ketones. Hydrazones are known to function as chelating agents²⁻⁴. The interest in such studies arises from the fact that these compounds can display antitubercular effects⁵, based on their tendency to form metal chelates with transition metal ions^{6,7}. The reaction of aroylhydrazones with transition metal ions can proceed according to two pathways attaining the ketonic (I) or enolic (II) structure for the hydrazide part of the molecule, as shown in Fig. 1 for copper ions.



Fig. 1. Ketonic (1) and Enolic (II) Structures of the Hydrazide Part of the Complexes with Copper Ions.

The mode of bonding was found to depend on the nature of both the ligand and metal ions^{8,9}, the anion of the metal salt and the solvent used^{10,11}. Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determinations of metal ions^{12,13}. Metal chelates of Co(II), Ni(II), Cu(II) and Zn(II) with some hydroxyphenylhydrazones were prepared by Osman and Ali¹⁴ The Cu and Zn complexes had square-planar or distorted tetrahedral structures. substituted aroylhydrazones The reactions of differently respectively. (RCH=NNHCOR) with Ni(II) and Cu(II) salts were investigated¹⁵. Ni(II) and Cu(II) acetates result in square-planar complexes with the ligands acting as monobasic acids coordinating as the enolic form. In case of Cu(II) chloride, reduction takes place and mono(aroylhydrazone) Cu(I) monochloride compounds were isolated.

The composition of the complexes of Cu, Co, Ni, Mn, Zn and Pb ions with 1-phenyl-3-methyl-4-(2-sulphophenylhydrazone)-5-pyrazolone in alcoholic solution was investigated spectrophotometrically¹⁶. CoCl₂.6H₂O and CuCl₂.2H₂O react with o-OHC₆H₄MeC=NNHCOR (R = Me, Ph, o-OHC₆H₄) to form 1:1 and 1:2 (metal : ligand) complexes for Cu(II), whereas 2:1 and 1:2 complexes were obtained for Co(II)¹⁷. Coordination in these complexes occurred through the carbonyl and azomethine groups, while the phenolic OH groups were not involved.

The present investigation deals with the preparation of new Cu(II) mandelic hydrazone derivatives. Attempts were made to prepare all chelates under investigation with Cu(II) acetate anhydrous. The resulting chelates were characterized using



 $X = m-OH (H_3L^1), p-OH (H_3L^2), o-Cl (H_2L^3), m-Cl (H_2L^4), p-Cl (H_2L^5), o-NO_2 (H_2L^6), m-NO_2 (H_2L^7), p-NO_2 (H_2L^8), p-N(CH_3)_2 (H_2L^9), o-OCH_3 (H_2L^{10}), p-OCH_3 (H_2L^{11}), 3,4-(OCH_3)_2 (H_2L^{12}) and p-CH_3 (H_2L^{13}).$

Fig. 2. Structure of the Mandelic Hydrazones.

elemental analyses, TG and DTA, IR, UV spectroscopy, X-ray diffraction and EPR spectra.

EXPERIMENTAL

All chemicals used in the present investigation were pure grade from BDH Chemicals. They included mandelic acid, hydrazine hydrate, benzaldehyde and some of its derivatives including m-, p-salicylaldehyde; o-, m-, p-Cl-benzaldehyde; m-Brbenzaldehyde; o-, m-, p-NO2-benzaldehyde; p-N(CH3)2-benzaldehyde; o-, panisaldehyde; 3,4-(OCH₃)₂-benzaldehyde and p-CH₃-benzaldehyde (p-tolylaldehyde), Cu(II) acetate anhydrous, ammonia, murexide indicator, ethylenediaminetetraacetic acid disodium salt (EDTA) and Nujol. The thermogravimetric analyses of the copper complexes with the mandelic hydrazone derivatives were carried out using a Netzsch Gerätebau 348472 C thermal analyzer. The weight loss was measured from ambient temperature up to 500° C at a rate of 5° C per minute. The infrared spectra were recorded using a Perkin-Elmer 983 double beam infrared spectrophotometer applying the KBr disc technique within the range 200-4000 cm⁻¹. The Nujol mull technique was applied to record the visible absorption spectra for the various complexes in the solid state (as solid suspensions), the spectra of the complexes were compared with those in saturated DMF solution. The visible spectra were recorded using a Perkin-Elmer Lamda 5 spectrophotometer.

Preparation of Mandelic Hydrazones

The mandelic hydrazones derivatives (HL¹-HL¹³) were prepared by the condensation of mandelic hydrazide (0.1 mole) with benzaldehyde derivatives^{18,19} (0.1 mole) in 100 mL ethanol as a solvent. After refluxing the mixture for about 1-4 h on a water bath, the respective hydrazones separated on cooling and were filtered, recrystallized from ethanol and then dried in a desiccator over silica gel. The results of microanalyses and physico-chemical data of the prepared hydrazones are listed in Table I.

Preparation of the Cu(II) Complexes

The metal complexes were prepared by mixing the ligand (0.01 and/or 0.02 mole) with Cu(II) acetate anhydrous (0.01 mole, 1.8164 g) in 100 mL ethanol. The mixture was refluxed for 6-24 h depending on the formation of the metal complex and the disappearance of the ligand. The solid complexes were precipitated on cooling, filtered, washed with ethanol and dried in a desiccator over silica gel.

RESULTS AND DISCUSSION

The results of elemental analyses of the solid Cu(II)-mandelic hydrazone complexes are recorded in Table II. From the data it can be shown that, the ligand H_3L^1 forms 1 : 1 and 1 : 2 (Cu^{2+} : L) complexes, whereas the ligands H_2L^3 and H_2L^5 form 2 : 1 and 1 : 1 (Cu^{2+} : L) complexes. The ligands $H_2L^7-H_2L^{13}$ form only 1 : 2 (Cu^{2+} : L) complexes. The ligand H_2L^6 (X = *o*-NO₂) forms a binuclear complex which has the stoichiometric ratio 2 : 1. In the 1 : 1 complexes, the mandelic hydrazones behave as dibasic tridentate ligands towards the Cu(II) ion, whereas, in the case of the 1 : 2 (Cu^{2+} : L) complexes they behave as monobasic bidentate ones. In the binuclear complexes, the organic compounds behave as dibasic tridentate ligands towards the Cu(II) ions. In binuclear Cu(II) complexes, the coordinated nature of acetate ion is supported by the addition of FeCl₃ solution to the complex solution where no redbrown color, characteristic of the iron-acetate complex, is observed. The calculated and found values of elemental microanalyses are in good agreement with each other,

						%С	%Н	%N
	Empirical	Formula	%			Found	Found	Found
Cpd.	formula	weight	Yield	Color	M.P. °C	Calc.	Calc.	Calc.
H ₃ L ¹	C15H14N2O3	270	80	white	179	66.94	5.02	10.33
	15 (4 2 5]				66.67	5.19	10.37
H ₃ L ²	C ₁₅ H ₁₄ N ₂ O ₃	270	65	white	240-241	66.46	5.49	10.91
						66.67	5.19	10.37
H ₂ L ³	C ₁₅ H ₁₃ N ₂ O ₂ Cl	288,5	70	white	172-173	62.62	4.28	9.70
						62.39	4.51	9.71
H ₂ L ⁴	C ₁₅ H ₁₃ N ₂ O ₂ Cl	288.5	60	white	125-126	62.18	5,00	9.61
						62.39	4.51	9.71
H ₂ L ⁵	C ₁₅ H ₁₃ N ₂ O ₂ Cl	288.5	75	white	160-161	62.33	4.63	9.86
						62.39	4.51	9.71
H ₂ L ⁶	C ₁₅ H ₁₃ N ₃ O ₄	299	75	pale yellow	135-136	60.40	4.58	13.88
ļ		· · · · · · · · · · · · · · · · · · ·				60.20	4.35	14.05
H ₂ L ⁷	C ₁₅ H ₁₃ N ₃ O ₄	299	60	pale yellow	171	60.57	4.81	14.00
						60.20	4.35	14.05
H ₂ L ⁸	C ₁₅ H ₁₃ N ₃ O ₄	299	65	pale yellow	165-166	59.98	4.68	13.91
			ļ			60.20	4.35	14.05
H ₂ L ⁹	$C_{17}H_{19}N_3O_2$	297	80	pale yellow	164-165	69.05	6.72	13.86
						68.69	6.40	14.14
H ₂ L ¹⁰	C ₁₆ H ₁₆ N ₂ O ₃	284	75	pale yellow	130-131	66.82	6.09	9.63
						67.06	5.63	9,86
H ₂ L ¹¹	C ₁₆ H ₁₆ N ₂ O ₃	284	70	white	177-178	67.03	5.89	9.68
						67.06	5.63	9.86
H ₂ L ¹²	C ₁₇ H ₁₈ N ₂ O ₄	314	70	white	159-160	65.19	5.61	8.52
		1		1		64.97	5.73	8.92
H ₂ L ¹³	C ₁₆ H ₁₆ N ₂ O ₂	268	75	white	148-149	71.74	5.83	10.03
						71.64	5.97	10.45

Table I. Analytical Data of Mandelic Hydrazone Derivatives

2.0209 2.0188 2.0181 Biso 8av . • ÷ EPR data gx=g1 2.0331 2.0029 2.0106 2.0299 2.0077 2.0312 18=28 %Cu(II) Found 16.24 20.23 16.47 18.17 16.24 17.26 20.53 20.37 Calc. 18.22 20.37 16.04 17.34 16.41 16.41 9.93 9.69 Found Calc. 7.72 7.26 8.56 4.49 N% 4.49 6.89 7.07 7.12 4.47 7.41 8.43 7.44 8.01 4.61 7.61 7.24 Found Calc. H% 4.33 4.67 5.12 4.88 5.03 4.65 4.39 4.29 4.03 3.53 4.98 4.65 4.85 4.39 4.23 4.01 Found 47.09 51.50 44.15 51.85 49.17 44.19 44.17 46.62 46.69 54.92 51.90 44.27 51.52 55.31 48.91 46.51 %C Calc. Color y. b. y. B y. b. у. b. у. b. aio ġ. × à ≻ ьb %Yield 20 65 60 75 2 80 75 80 385.5 655.5 349.5 623.5 623.5 F.W. 386 396 368 2:1 M:L 2:1 1:1 1:2 Ξ Ξ 1:I Ξ $[Cu_2(L^3)(AcO)_2(EtOH)_2]$ $Cu_2C_{23}H_{29}N_2O_8CI$ [Cu₂(L⁵)(AcO)₂(EtOH)₂] Cu₂C₂₃H₂₉N₂O₈CI CuC₁₇H₁₇N₂O₃Cl CuC₁₅H₁₃N₂O₃Cl Cu15H15N2O4CI CuC₁₅H₂₀N₂O₆ CuC₃₀H₃₂N₄O₉ CuC₁₅H₁₄N₂O₄ Empricial Formula [Cu(HL¹)₂(H₂O)₂] H₂O [Cu(L⁵)H₂O] H₂O [Cu(HL¹)(H₂O)₃] [Cu(HL²)H₂O] [Cu(L³)EtOH] $[Cu(L^4)H_2O]$ Complex

Table II. Analytical and Electron Paramagnetic Resonance Data of Mandelic Hydrazone Cu(II) Complexes

[Cu ₂ (L ⁶)(AcO) ₂ (EtOH) ₂]	Cu ₂ C ₂₃ H ₂₉ N ₃ O ₁₀	2:1	634	80	þ.	43.97 43.53	4.24 4.57	6.55 6.62	20.14 20.03	2.0227	2.0053		2.0140
[Cu(L ⁷)EtOH] H ₂ O	CuC ₁₇ 11 ₁₉ N ₃ O ₆	1:1	424.5	75	г. b.	48.27 48.06	4.85 4.48	10.03 9.89	15.05 14.96				
[Cu(L ⁸)(H ₂ 0) ₂ EtOH]	CuC ₁₇ H ₂ 1N ₃ O ₇	1:1	442.5	65	ġ.	46.78 46.10	4.85 4.75	8.94 9.49	14.65 14.35	2.0336	2.0058	2.0136	2.0177
[Cu(L ⁹)H ₂ O]	CuC ₁₇ H ₁₉ N ₃ O ₃	1:1	376.5	70	y. b.	54.74 54.18	5.60 5.05	10.91 11.16	16.45 16.87				
[Cu(L ¹⁰)EtOH]	CuC ₁₈ H ₂₀ N ₂ O ₄	1:1	391.5	80	a	55.69 55.17	4.77 5.11	6.87 7.15	16.10 16.22				
[Cu(L ¹¹)H ₂ O]	CuC ₁₆ H ₁₆ N ₂ O ₄	1:1	363.5	75	y. g	53.13 52.82	4.27 4.40	7.49 7.70	17.30 17.47				
[Cu(L ¹²)H ₂ 0]	Cu C ₁₇ H ₁₈ N ₂ O ₅	1:1	393.5	70	×.	51.69 51.84	4.75 4.57	7.48 7.12	16.16 16.14				
[Cu(L ¹³)H ₂ 0]	CuC ₁₆ H ₁₆ N ₂ O ₃	1:1	347.5	65	sia X	54.86 55.25	4.63 4.60	7.98 8.06	18.23 18.27				

y.g. : yellowish green, g.b. : greenish brown, y.b. : yellowish brown, b.y. : brownish yellow, b: brown, r.b. : reddish brown, g.y. greenish yellow, y.: yellow. indicating that the suggested molecular formulae recorded in Table II are correct. It is also noted that all prepared complexes are associated with coordinated water or ethyl alcohol molecules which are not removed by applying a static 1 mm Hg. vacuum for 2-3 hours.

Thermogravimetric and Differential Thermal Analyses

Thermal methods of analysis open a new possibility for the investigation of metal chelates^{20,21}. The aim of this study is to obtain information concerning the thermal stability of the investigated chelates, decide whether the water or alcohol molecules are in the inner or outer coordination sphere of the central metal ion. From TG curves one can calculate the percentage of water or alcohol molecules and metal ions in the chelates, whereas the DTA data make it possible to characterize thermographically the process of phase transformation in the examined system. To understand the mechanism of complex formation and the stability of the complexes so formed, it is of interest to observe the intermediate products formed by oxidative action and heat on the investigated metal complexes. In the thermograms of the [Cu(IIL¹)(H₂O)₃], [Cu₂(L⁶)(AcO)₂(EtOH)₂] and [Cu(L⁹)H₂O] complexes, the first part of the thermogram shows the removal of water or ethyl alcohol molecules from the complexes under investigation within the temperature range 50-255° C. The anhydrous or unsolvated complex shows thermal stability up to 200-300° C. In the case of the $[Cu_2(L^6)(AcO)_2(EtOH)_2]$ complex, the acetic acid molecules are expelled at 255-265° C. The decomposition of the complex to Cu2O starts within the temperature range 275-300° C. The DTA curves of the investigated chelates show endothermic peaks within the range 220-255° C due to the removal of coordinated water and/or ethyl alcohol molecules.

At higher temperature, some lattice rearrangements are observed at the beginning of the melting of the anhydrous complex followed by a phase tranformation accompanying the oxidation of organic products. Finally, the thermal decomposition leads to the formation of the final product which was found to be Cu_2O . The percentage losses in weight of the complexes, calculated from the inflections on the TG curves, are given in Table III. From this table one can see that the

Decomposition and formation of Cu₂O Decomposition and formation of Cu₂O Decomposition and formation of Cu₂O One acetic acid molecule (AcOH) One acetic acid molecule (AcOH) Coordinated EtOH Coordinated EtOH Coordinated H₂O Coordinated H₂O Coordinated H₂O Coordinated H₂O Thermal stability Thermal stability Thermal stability Assignment 23.82 33.12 Calc. 14.01 9.34 7.26 14.51 4.67 4.78 ٠ ٢ . ۱ ī ı. % Loss Found 14.37 33.59 14.31 4.58 9.38 7.35 23.81 4.99 ī. ı. ı. ı. ï ı. DTA Exo. 275 220 240 250 255 ı ı. ī ı. ı t ı ī Thermal step 220-240 240-280 280-300 250-255 50-220 50-250 255-260 260-265 265-275 250-290 50-250 275 ŋŢ 300 290 ပ္ Temperature, Cu-lig. core Temp. 300 275 290 Decomp. lnit. 50 50 50 Cu₂(L⁶)(AcO)₂(EtOH)₂] $Cu_2(L^6)(AcO)_2.EtOH]$ Complex $Cu(HL^{1})(H_{2}O)_{3}]$ $[Cu(HL^1)(H_2O)_2]$ $[\mathrm{Cu}_2(\mathrm{L}^6)(\mathrm{AcO})_2]$ [Cu₂(L⁶).(AcO)] $[Cu(HL^1),H_2O]$ [Cu(1.⁹).H₂O] [Cu(HL¹)] [Cu₂(L⁶)] $[Cu(L^9)]$

Table III. Thermogravimetric and Differential Thermal Temperature, °C Analysis of Some Mandelic Hydrazone Cu(II) Complexes

Cu(II) COMPLEXES WITH NEW MANDELIC HYDRAZONES

 $[Cu(HL^1)(H_2O)_3]$ complex has the highest thermal stability among the complexes under investigation; also the thermal stability increases in the order $[Cu(HL^1)(H_2O)_3]$ $< [Cu(L^9)H_2O] < [Cu(L^6)(AcO)_2(EtOH)_2].$

The stability runs parallel with the following electronic substituent effect of hydrazone ligands in the order: $p-N(CH_3)_2$ (H₂L⁹) > $o-NO_2$ (H₂L⁶).

Infrared Spectra

The assignment of the diagnostic infrared bands of the mandelic hydrazonecopper (II) complexes are depicted in Table IV.

On examing the infrared spectra of the Cu(II) complexes, in comparison to those of the corresponding free ligands, the following can be pointed out. The spectra of all complexes exhibit a broad band around 3520-3400 cm⁻¹ which is attributed to v(OH) of water and/or EtOH molecules associated with the central Cu(II) ion in the complex. In the 1 : 1 complexes the infrared spectra of the Cu(II) complexes with the ligands HL¹-HL⁵ and HL⁷-HL¹³ have the same general features. The v(OH) alcoholic and v(OH) enolic bands in the spectra of free ligands disappeared when these ligands reacted with Cu(II) ion. The bands corresponding to δ (OH) and γ (OH) in the spectra of the free mandelic hydrazones are absent in the spectra of the Cu(II) complexes. The disappearance of the δ (OH) and γ (C-OH) bands in the spectra of the complexes can be ascribed to the displacement of two protons, from the alcoholic and enolic OH groups of the free hydrazones by the Cu(II) ion leading to covalent linkage with these ligands. Also, the v(C=N) band is split into two bands at 1650-1620 cm⁻¹ and 1600-1580 cm⁻¹ due to free and coordinated C=N groups, respectively.

Support of the above interpretation is the appearance of the non-ligand bands v(M - O) and v(M - N) at 557-400 cm⁻¹ and 380-316 cm⁻¹, respectively.

The mode of bonding in the (1 : 2) Cu-HL¹ complex, as shown from its infrared spectrum (Table IV), can be explained by the following: the v(OH) enolic group in the spectrum of the free ligands is not observed in the spectrum of the Cu(II) complex while the v(OH) of the alcoholic group in the free hydrazone is still observed at the same position in the spectrum of the Cu(II) complex. Support for this behaviour is

780 600 630 710 740 700 715 650 750 670 740 635 870, 750 760 800, 700 UV-visible; λ nm Nujol 860, 860, 860, 810, 810, 810, 810, 800, 800, 820. 860, 810. 860, DMF 650 580 600 650 590 600 650 600 600 520 600 550 650 525 500 $v_{\mathcal{S}}$ (COO) v(M-O) v(M-N)cm⁻¹ cm⁻¹ cm⁻¹ 316 357 367 360 360 355 328 375 360 357 380 340 370 339 375 468 455 460 548 557 450 460 400 539 450 527 509 480 541 490 1439 1445 1444 ı. ÷ ı. , ı. ł ı. ÷ . . ı. . , v(C=N) v(C=N) v_{as} (COO) cm^{-1} cm^{-1} 1546 1547 1522 ı. 1 ŧ. ı. т. . ı. 1 . ١ ı. ı. . 1595sh 1590sh 1595sh coord. 1590 1590 1600 1580 1598 1600 1595 1600 1590 1585 1595 1587 1640sh 1625sh 1640sh 1630sh 1650sh 1525sh 1460sh 1640sh l 640sh 1638 1620 1650 1620 1638 1525 free H₂O/EtOH 3520sh v(OH) cm⁻¹ 3400 3420 3420 3450 3440 3438 3417 3430 3407 3425 3420 3440 3410 3442 Ratio M:L $\overline{\ldots}$ Ξ П Ξ E Ξ Ξ E Ξ Ξ Ξ 2:1 5 2:1 $[Cu_2(L^3)(AcO)_2(EtOH)_2]$ $[Cu_2(L^5)(AcO)_2(EtOH)_2]$ $[Cu_2(L^6)(AcO)_2(EtOH)_2]$ $[Cu(L^8)(H_2O)_2.EtOH]$ $[Cu(L^7).EtOH] H_2O$ $[Cu(L^5).H_2O] H_2O$ $Cu(HL^{1})(H_{2}O)_{3}$ $[Cu(HL^2), H_2O]$ [Cu(L¹⁰).EtOH] $[Cu(L^{11}),H_2O]$ [Cu(L³).EtOH] [Cu(L¹²).H₂O] [Cu(L¹³).H₂O] $Cu(L^4).H_2O$ $[Cu(L^9), H_2O]$ Complex

Table IV. Assignment of Infrared and UV-Visible Spectral Data of Mandelic Hydrazone Cu(II) Complexes

gained from the observed decrease in the intensity of $\delta(OH)$ at 1331 cm⁻¹ and $\gamma(C-OH)$ at 1059 cm⁻¹ in the case of the Cu(II) complex in comparison with those of the free hydrazones. This indicates that the enolic group participates in complex formation in the 1 : 2 (Cu²⁺ : L) complex. The v(C=N) band of the free hydrazones is split into two bands located at 1660 cm⁻¹ and 1605 cm⁻¹ in the spectra of the Cu(II) complex, corresponding to free and coordinated C=N groups, respectively. Support for the above interpretation is the appearance of non-ligand bands at 530 and 420 cm⁻¹ due to v(M—O) and v(M—N), respectively.

In the case of the 2 : 1 (Cu²⁺ : L) binuclear complexes of the ligands H₂L³. H₂L⁵ and H₂L⁶, the v(OH) phenolic and v(OH) enolic bands located at 3420 and 3400 cm⁻¹ and 3070-3045 cm⁻¹, respectively, in the spectra of the free ligand disappeared when these ligands reacted with Cu(II) ion. Also, the δ OH) and γ (C-OH) bands located in the spectra of the free ligands at 1360-1258 cm⁻¹ and 1064-1058 cm⁻¹ are absent in the spectra of the Cu(II)-complexes. The C=N bands in the spectra of these complexes are also split into two bands due to the free C=N group at 1640-1638 cm⁻¹ and the coordinated C=N group at 1595-1585 cm⁻¹. The four new bands observed in the spectra of the Cu(II) complexes (absent in the spectra of the free hydrazones) located at 1549-1522, 1446-1439, 527-460 and 575-339 cm⁻¹ are due to v_{as}(COO), v_s(COO), v(M-O) and v(M-N), respectively. The first two bands indicate the coordinated nature of the acetate ion as bidentate ligand²².

Electronic Absorption Spectra of Cu(II)-Mandelic Hydrazone Complexes

Based on the fact that electronic absorption spectra are very diagnostic of the stereochemistry of the metal complexes, the electronic spectra of the solid complexes prepared in this work were measured as Nujol mulls and in solution using DMF as a solvent. Most of the solid complexes prepared have a limited solubility in DMF, hence, the Nujol mull technique is applied in order to obtain the visible absorption spectra for the various complexes as solid suspensions. Thus, the crystal form of the investigated samples cannot be destroyed as when using solvents. The majority of the six-coordinated Cu(II) complexes are tetragonally distorted and their spectra exhibit

one absorption band in the visible region at ≥ 650 nm, whereas the square-planar structure shows a broad band around the range of 625-700 nm²³. From the data in Table IV, slight differences between the Nujol mull spectra of the solid complexes and the spectra of the complexes in DMF solution are observed. The electronic absorption spectra of the Cu(II) complexes under investigation show one or two broad bands with λ_{max} at 580-650 and 875-775 nm for the mandelic hydrazone-Cu(II) complexes. The ligands HL¹, HL², HL⁶ and HL⁸ give Cu(II) complexes with tetragonal, elongated-octahedral as well as square-planar symmetries. The electronic transitions for the last two bands may be assigned to the ${}^{2}B_{1g} \rightarrow {}^{2}B_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions, respectively, whereas the ligands H₃L², H₂L⁴, H₂L⁷, H₂L⁹, H₂L¹⁰, H₂L¹¹, H₂L¹² and H₂L¹³ possess tetrahedral geometry around the Cu(II) ion.

The electronic transition leading to the two bands at 780-600 nm and 870-800 nm can be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \rightarrow {}^{2}B_{1g}$ transitions, respectively. It is interesting to mention that the HL³- and HL⁵-Cu(II) complexes possess two symmetries, tetrahedral geometry around Cu(II) ion for the 1 : 1 complexes and square-planar for the 2 : 1 (M : L) complexes.

X-Ray Diffraction Patterns of Cu(II)-Mandelic Hydrazone Complexes

The interplanar spacing (d, Å) and the relative intensities (I/I) of the Cu(II) complexes with mandelic hydrazones, $[Cu_2(L^5)(AcO)_2(EtOH)_2]$, $[Cu(L^8)(H_2O)_2EtOH]$ and $[Cu(L^{13})H_2O]$, were calculated and recorded in Table V. On comparing the X-ray diffraction patterns of each hydrazone with its corresponding Cu(II) complex, the following can be pointed out:

i) The diffraction patterns of the Cu(II) complexes differ in the interplanar distances (d, Å) and relative intensities from those of the corresponding ligand, thus indicating complex formation.

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 fine crystallite size and the deformations occurring in the crystal lattice.

This can be ascribed to the possible orientation of the ligand molecules or distortion of the coordination polyhedron around the Cu(II) ion²¹. The changes in

 $\begin{array}{c|c} [Cu(L^{13})H_2O] \\ \hline d(Å) & I/\mathring{l} \end{array}$ 9 15 13 × Ξ 17 70 100 22 22 34 4 60 Ξ 23 10.16 4.42 5.15 5.10 4.75 4.58 13.81 12.81 9.11 6.92 6.33 5.68 5.43 5.34 5.91 $\begin{array}{|c|c|c|}\hline [Cu(L^8)(H_2O)_2EtOH] \\ \hline d(Å) & U^{\dagger}_{1} \end{array}$ 16 32 35 4 × 13 26 26 9 001 12 4 22 21 41 13.60 12.63 8.43 6.86 6.28 5.99 5.83 5.37 5.07 4.58 4.17 4.00 3.83 4.31 9.31 $\frac{\left[Cu_{2}(L^{5})(AcO)_{2}(EtOH)_{2}\right]}{d(A)}$ 48 6 6 24 14 26 15 15 16 33 47 100 15 22 30 10.05 d(Å) 12.63 7.14 6.92 6.42 6.15 5.10 4.75 4.55 5.95 5.75 4.67 8.85 6.71 5.41 5 $\frac{H_2L^{13}}{d(Å)} \frac{1/\mathring{I}}{1/\mathring{I}}$ Ś 2 6 100 27 1 15 Ξ 18 16 20 34 34 51 13.81 10.78 85 5.95 5.47 5.16 4.98 4.85 4.77 4.46 4.40 4.23 4.15 4.00 6.81 οò. 17 10 6 19 58 <u>_</u> 1 24 20 26 25 $\frac{H_2L^8}{d(A) \mid I \hat{N}}$ 33 32 21 61 13.60 10.92 5.16 5.57 4.90 4.72 4.40 4.23 4.08 4.00 74 3.61 5.41 48 5.91 4 ŝ $\frac{H_2L^5}{M_1M_1}$ 10 × 50 50 6 4 13 so 2 Ξ 22 25 Ξ 21 47 13.39 10.78 5.44 5.16 5.04 4.82 4.40 4.15 4.08 3.97 3.80 3.63 3.55 3.48 5.91 d(Å)

Table V. X-ray Diffraction Data of some Mandelic Hydrazones and their Cu(II) Complexes

_			<u> </u>	_					-						
27	25	23	11	Ξ	13	26	15	6	∞	10	10	6	6	8	9
4.35	4.27	4.19	4.00	3.87	3.58	3.40	3.26	3.16	3.06	3.00	2.96	2.94	2.87	2.73	2.55
14	21	18	13	6	14	6	6	10	×	5	\$	5	7	9	I
3.74	3.66	3.59	3.53	3.34	3.23	3.12	3.10	2.98	2.88	2.79	2.70	2.48	2.31	2.08	•
29	30	47	29	30	30	16	15	12	19	30	14	19	12	6	6
4.40	4.26	4.55	4.40	4.27	4.15	3.93	3.87	3.74	3.56	3.43	3.30	3.23	3.14	3.06	2.71
56	8	6	Ξ	=	Ξ	9	5	23	6	é,	7	6	.c	9	•
3.80	3.65	3.59	3.53	3.45	3.19	3.10	3.04	2.93	~i	2.78	2.74	2.70	2.58	2.47	
6	100	33	17	21	13	14	∞	9	Ξ	6	5	S	Ś		
3.55	3.38	3.30	3.19	2.93	2.80	2.71	2.67	2.55	2.46	2.31	2,12	1.99	1.93	ı	
100	Ξ	9	12	7	26	7	7	10	10	6	5	1	•	•	1
3.35	3.30	3.23	3.16	3.09	2.92	2.81	2.78	2.71	2.61	2.47	2.40	'	1	•	

d, Å and I/I in the mandelic hydrazone Cu(II) complexes may be attributed to different structures *i.e.*, involvement of a number of lattice or coordinated water/ethanol molecules, the different orientations of the ligands around the central Cu(II) ion²⁴, the various spherical rotations around the lattice axes, diffraction planes and transition group operations^{25,26}.

Electron Paramagnetic Resonance (EPR) Spectra

EPR spectra at room temperature of some of the Cu(II) complexes under investigation 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)-environments are given in Table II. The g_{iso} value in the case of the [Cu(HL¹)(H₂O)₃] complex relative to the other complexes could be attributed to a different electron-donating effect of the groups attached to the hydrazone benzene ring. Generally, these compounds are not magnetically dilute; therefore, exchange²⁷ and/or dipolar forces are expected to operate, in which case, the g anisotropy is likely to be reduced. The absence of hyperfine splitting in the [Cu(L³)EtOH] complex is taken as evidence of exchange, as is the fact that $G = g// - 2/g \perp -2$ is lower than 4²⁸ which could be attributed to tetrahedral symmetry around the Cu(II) ion. Moreover, the apparent broadening of the EPR signals may be due to an interaction between Cu(II) ions which are probably in non-equivalent lattice positions.

Based on the above results gained from the elemental analyses, IR, electronic, X-ray diffraction as well as EPR spectra, the structure of the 1 : 1 complexes formed between Cu(II) ion and the ligands under investigation where X = p-OH, *o*-. *m*-, *p*-Cl, *o*-, *m*-NO₂, *p*-N(CH₃)₂, *o*-, *p*-OCH₃, 3,4-(OCH₃)₂ and *p*-CH₃ may be represented by a tetrahedral geometry around the Cu(II) ion as shown in Fig. 3. These complexes are [Cu(HL²)H₂O], [Cu(L³)EtOH], [Cu(L⁴)H₂O], [Cu(L⁵)H₂O]H₂O, [Cu(L⁷)EtOH]H₂O, [Cu(L⁹)H₂O], [Cu(L¹⁰)EtOH], [Cu(L¹¹)H₂O], [Cu(L¹²)H₂O] and [Cu(L¹³)H₂O]. The complexes [Cu(HL¹)(H₂O)₃] and [Cu(L⁸)(H₂O)₂EtOH] have a tetragonal distorted-octahedral geometry around Cu(II) ion. The 1 : 2 (M : L) complex of the



 $S = H_2O$ or EtOH

Fig. 3. The Structural Formula of the 1 : 1 Complexes Formed Between Cu(II) lons and the Mandelic Hydrazones.



Fig. 4. The 1:2 Complexes of Cu(II) Ions with the Mandelic Hydrazones.



Fig. 5. The Binuclear Complexes of Cu(II) lons with the Mandelic Hydrazones.

form $[Cu(HL^1)_2(H_2O)_2]H_2O$ has a distorted octahedral geometry around the Cu(II) ion as shown in Fig. 4.

The binuclear complexes $[Cu_2(L^3)(AcO)_2(EtOH)_2]$, $[Cu_2(L^5)(AcO)_2(EtOH)_2]$ and $[Cu(L^6)(AcO)_2(EtOH)_2]$ have a square-planar structure, as shown in Fig. 5.

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