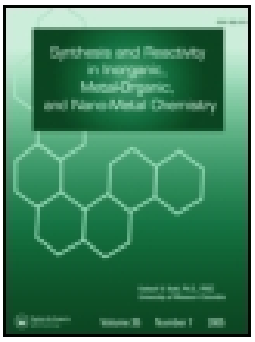

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LIGATIONAL BEHAVIOUR OF ELECTROCHEMICALLY SYNTHESIZED COPPER(II) COMPLEXES OF DIETHYL 2,3-DIOXOPENTANEDIOATE-2-ARYLHYDRAZONE DERIVATIVES

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ABSTRACT

Cu(II) complexes of diethyl 2,3-dioxopentanedioate-2-arylhydrazone derivatives have been prepared electrochemically. Their ligational behaviour has been studied using elemental analyses, IR and electronic spectra, magnetic moments and thermogravimetric studies. This work revealed that the structure of the synthesized complexes and their spectral behavior depend, to some extent, on the type and nature of substituents on each ligand. The arylhydrazones under investigation act as α-arylhydrazone ester as well as β-keto ester. Electronic spectra suggest a square-planar structure of the complexes.

INTRODUCTION

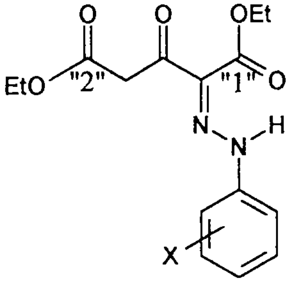
Dinuclear copper complexes have found increasing interest in many fields of chemistry[1]. Copper ions play important roles in a number of enzyme systems[2], and coupled copper active sites are present in a wide variety of them[3]. Many studies are being carried out to develop dinuclear copper complex models. On the other hand, arylhydrazones and their metal complexes are characterized by considerable significance and importance due to their numerous applications as chemotherapeutic agents[4], insecticides[5], chromogenic reagents[6], photoreceptors in electrophotography and also in analytical chemistry[7]. Many studies are concerned with dinucleating ligands, particularly on the spin-spin exchange interaction between metal ions[8]. The purpose of this study is the preparation of dinuclear copper(II) complexes with ligands containing two separate chelating centers. Thus, 2,3-dioxopentanedioate-2-arylhydrazone derivatives, as a new class of ligands, may act as α-arylhydrazone ester and β-keto ester. A literature survey revealed that no work has been done on the ligational properties of the ligands represented in Fig. 1.

A variety of synthetic pathways have been reported for the preparation of metal arylhydrazone complexes involving reaction of arylhydrazones with metal salt solutions in a suitable solvent. But the preparation of the ester complexes is difficult using the usual chemical methods[9]. The direct electrochemical synthesis using a sacrificial anode has been the subject of some recent work[10-12]. The method is simple, may be carried out at room temperature by using unsophisticated apparatus and gives highly pure products in good yield.

EXPERIMENTAL

Preparation of the Ligands

Diethyl 2,3-dioxopentanedioate-2-arylhydrazones (H_2L^{a-i}) have been prepared by coupling of an ice-cooled solution of diethyl 3-oxopentanedioate (10.1 g, 50 mmol) in ethanol (200 mL) containing sodium acetate trihydrate (35 g) and adding an equimolar amount of the appropriate diazotized aromatic amine gradually with continuos stirring. The reaction mixture was kept for 1 h at 0-5° C, diluted with water and the obtained solid was collected. The resulting solids were crystallized from the appropriate solvents: $\mathbf{H_2L^a}$, m.p. 60° (pet.



X = p-OCH_3 (H_2L^a), p-CH_3 (H_2L^b), p-Br (H_2L^c), p-Cl (H_2L^d), o-COOH (H_3L^e), o-$COOCH_3$ (H_2L^f), o-NO_2 (H_2L^g), p-NO_2 (H_2L^h), o-OH (H_3L^i);
"1" = ester group 1, "2" = ester group 2.

Fig. 1. Structure of the Ligands

ether); $\mathbf{H_2L^b}$, 80° (EtOH); $\mathbf{H_2L^c}$, 90° (pet. ether); $\mathbf{H_2L^d}$; 79° (pet. ether); $\mathbf{H_3L^e}$, 144° (MeOH); $\mathbf{H_2L^f}$, 89° (EtOH); $\mathbf{H_2L^g}$, 125° (EtOH); $\mathbf{H_2L^h}$, 108° (EtOH); $\mathbf{H_3L^i}$, 139° (EtOH). The *p*-tolyl, *p*-nitro and *o*-carboxy derivatives have been previously prepared by Bülow[13]. All used materials are of high purity from Aldrich chemical company.

Preparation of the Cu(II) Complexes

The electrochemical cell consisted of a beaker (100 mL) fitted with a rubber cover through which the electrochemical leads are passed. The cathode was a Pt wire. The copper anode was immersed in the solution by a Pt wire. 1 mmole of ligand was dissolved in 50 mL pure dry acetone. The current ranged from 8-16 mA depending on the number of equivalents required for each complex, which in turn depended on the number of replaceable protons. In the case of an insufficient current flow, cetyltrimethylammonium bromide was added to the solution phase as supporting electrolyte. The current was controlled throughout the electrolysis. The required time of electrolysis was calculated from Faraday's equation. It should be mentioned that H_2 gas was evolved at the cathode during the reaction. After the calculated time the solution was concentrated by evaporation on a water bath, then diluted with distilled water. The precipitated product was collected, washed with ethanol/water (50% v/v) till the filtrate was colourless. The yields ranged from 60-70%.

Measurements

Elemental analyses were performed at the Microanalytical Center of Cairo University. Copper ions were analyzed complexometrically using murexide as indicator according to the standard procedure[14]. IR spectra of the ligands and their Cu(II) complexes (KBr discs) were recorded on a Pye Unicam SP 3-300 spectrophotometer. Electronic spectra of the complexes were obtained in dimethylformamide with the aid of a Perkin Elmer Lambda 4B spectrophotometer. Magnetic moments were recorded using a Sherwood Scientific Magnetic Susceptibility Balance at room temperature (25° C) and $Hg[Co(SCN)_4]$ as calibrant. Thermal analyses were carried out using TG-50 and DTA-50 Shimadzu instruments in N_2 from ambient temperature up to 800° C at a heating rate of 10° C/min.

RESULTS AND DISCUSSION

The electrochemical reactions may be represented by the following equations:

$$2Cu \rightarrow 4e^- + 2Cu^{2+}$$

$$H_2L + 2e^- \rightarrow L^{2-} + H_2\uparrow$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$$

$$\underline{2Cu^{2+} + L^{2-} + 2OH^- + nH_2O \rightarrow Cu_2L(OH)_2.nH_2O}$$

$$2Cu + H_2L + (n+2)\,H_2O \rightarrow Cu_2L(OH)_2.nH_2O + 2H_2\uparrow$$

All prepared complexes have high melting points, are quite stable at room temperature and can be stored for a long period without changes in their composition. The electrochemical oxidation of copper in acetone solutions of the ligands gives complexes with the stoichiometric ratios represented in Table I which are in good agreement with the results of elemental analyses.

IR Spectral Studies of Ligands and Metal Chelates

For elucidating the structure of the Cu(II) complexes the IR spectra of the solid complexes, Table II, were compared with those of the corresponding free ligands.

The IR spectra of the ligands $H_2L^{a\text{-}i}$ show a broad ν(NH) band at 3196-3112 cm^{-1}, ν(C=O) bands appearing as two or three sharp bands at 1730, 1690 and/or 1670 cm^{-1}, the first is attributed to ν(C=O) of the unconjugated ester group (ester group 2) while the latter two bands correspond to both ketonic and conjugated ester (ester group 1) carbonyls. The lowering in frequency of the latter bands may be attributed to intramolecular hydrogen bonding between the ketonic C=O and NH groups and the conjugation of the carbonyl ester with the C=N linkage. The characteristic CH bending vibration band of the $-CH_2CO-$ moiety for the ligands appears at 1400-1440 cm^{-1}.

The IR spectra of the complexes confirmed the presence of H_2O molecules in some complexes by the appearance of ν(OH) as a broad, strong band at 3434-3364 cm^{-1} assigned to both OH of coordinated water molecules and OH ions that complete the coordination sphere of the complexes. A strong sharp band at 1270-1248 cm^{-1} is due to δ(OH) and the band at 615-701 cm^{-1}

Table I. Characterization Data of the Cu(II) Complexes

Chelate Empirical Formula	Formula Weight (Yield %)	M.p. °C	Calcd./(found) %			
			C	H	N	Cu
$[Cu_2L^a(OH)_2H_2O(CH_3)_2CO]$ $C_{19}H_{28}N_2O_{10}Cu_2$	571.43 (50)	225	39.90 (39.80)	4.90 (4.80)	4.90 (4.70)	22.22 (22.31)
$[Cu_2L^b(OH)_2(H_2O)_2]$ $C_{16}H_{24}N_2O_9Cu_2$	515.37 (55)	>350	37.25 (37.60)	4.66 (5.00)	5.43 (5.30)	24.64 (25.15)
$[Cu_2L^c(OH)_2((CH_3)_2CO)_2]^a$ $C_{21}H_{29}N_2O_9BrCu_2$	660.37 (48)	210	38.16 (38.10)	4.39 (4.30)	4.24 (4.00)	19.23 (20.78)
$[Cu_2L^d(OH)_2((CH_3)_2CO)_2]^b$ $C_{21}H_{29}N_2O_9ClCu_2$	615.91 (62)	190	40.92 (40.90)	4.71 (3.40)	4.55 (4.40)	20.62 (20.31)
$[Cu(HL^d)_2]^c$ $C_{30}H_{32}N_4O_{10}Cl_2Cu$	743.03 (50)	150	48.45 (48.90)	4.31 (4.20)	7.54 (6.50)	8.55 (8.93)
$[Cu_2L^e(OH)(H_2O)_2]$ $C_{16}H_{20}N_2O_{10}Cu_2$	527.33 (49)	240	36.41 (36.80)	3.79 (4.10)	5.31 (5.00)	24.08 (24.53)
$[Cu_2L^f(OH)_2(H_2O)]$ $C_{17}H_{22}N_2O_{10}Cu_2$	541.36 (63)	247	37.68 (37.30)	4.06 (3.90)	5.17 (5.20)	23.46 (23.16)
$[Cu_2L^g(OH)_2(CH_3)_2CO]$ $C_{18}H_{23}N_3O_{10}Cu_2$	568.39 (67)	>350	38.00 (37.96)	4.05 (3.80)	7.39 (7.60)	22.34 (22.68)
$[CuL^h(H_2O)(CH_3)_2CO]$ $C_{18}H_{23}N_3O_9Cu$	488.89 (55)	263	44.18 (43.70)	4.70 (4.80)	8.59 (7.90)	12.99 (13.25)
$[Cu_2L^I_2]$ $C_{30}H_{32}N_4O_{12}Cu_2$	767.58 (70)	245	46.90 (46.50)	4.17 (3.70)	7.30 (6.90)	16.55 (16.89)

[a] Br %: 12.12 (12.30); [b] Cl %: 5.76 (5.90); [c] Cl %: 9.56 (9.20).

Table II. Magnetic, IR and UV-Vis.Data of the Cu(II) Complexes

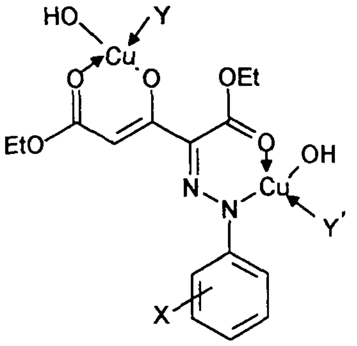
Formula	μ_{eff}	IR bands assignment[a]						Electronic bands	
	B.M.	ν(OH)	δ(OH)	$\rho_r(H_2O)$	ν(C=O)	Cu-N	Cu-O	cm^{-1}	ε values
$[Cu_2L^a(OH)_2H_2O(CH_3)_2CO]$	1.27	3434 broad	1248 m	618 w	1695 m	---	---	--- 34014	--- 1.08
$[Cu_2L^b(OH)_2(H_2O)_2]$	1.58	3393 broad	1254 m	615 w	1691 m	484 w	---	20703 33898	0.41 0.99
$[Cu_2L^c(OH)_2((CH_3)_2CO)_2]$	1.31	3409 broad	---	---	1695 m	503 w	406 w	21978 33670	0.40 1.06
$[Cu_2L^d(OH)_2((CH_3)_2CO)_2]$	1.44	3400 broad	---	---	1706 m	468 w	434 w	27203 33704	1.39 1.16
$[Cu(HL^d)_2]$	1.87	---	---	---	1706 m	---	434 w	27640 33058	1.39 1.16
$[Cu_2L^e(OH)(H_2O)_2]$	1.61	3380 broad	1259 m	700 w	1700 m	496 w	---	25368 33704	0.79 0.71
$[Cu_2L^f(OH)_2(H_2O)]$	1.45	3364 broad	1258 m	701 w	1729 m	499 w	---	24612 33704	0.99 0.84
$[Cu_2L^g(OH)_2(CH_3)_2CO]$	1.36	3414 broad	---	---	1720 m	469 w	---	--- 32123	--- 0.98
$[CuL^h(H_2O)(CH_3)_2CO]$	1.82	3432 broad	1270 m	695 w	1700 m	493 w	---	19146 25654 33887	1.96 1.25 1.11
$[Cu_2L^i_2]$	1.43	---	---	---	1725 s 1693 m	474 w	409 w	20717 26925 33523	1.03 0.59 0.60

[a] s = strong, m = medium, w = weak.

may be assigned to $\rho_r(OH)$[15], providing additional evidence for coordinated water molecules. It is worth to mention that the $\delta(OH)$ and $\rho_r(OH)$ bands have not been observed in the spectra of the complexes where only acetone molecules have completed their coordination spheres.

The ligands H_2L^{a-d} behave as dinuclear dibasic tetradentate ligands towards Cu(II) ions, coordinating via NH and CO (ester group 1) on one side and the enolic OH and CO (ester group 2) on the other side. The appearance of only one medium $\nu(C=O)$ band at lower frequency, 1700-1691 cm^{-1}, emphasizes the participation of the carbonyl groups in complexation. The $\delta(CH)$ band at 1400-1440 cm^{-1} of the free ligands disappeared whereas a new band in the complexes was observed at 1052-1028 cm^{-1} assigned to $\nu(C-O)$ formed as a result of enolization and subsequent coordination. The broad OH band masked the $\nu(NH)$ band of the free ligands. From the above results the proposed formula of the Cu(II)-H_2L^{a-d} complexes can be represented by the structure in Fig. 2.

IR spectra of the *o*-carboxy derivative (H_3L^e) revealed that this ligand behaves as a dinuclear, tribasic, pentadentate ligand towards the two Cu(II) ions coordinating via the NH, OH (carboxylic) and CO (ester group 1) on one side and enolic OH, CO (ester group 2) on the other side. The proposed structure of the $[Cu_2L^e(OH)(H_2O)_2]$ complex is confirmed by 1) the appearance of a broad band at 3550-3050 cm^{-1} which is assigned to $\nu(OH)$ of H_2O and the OH group that complete the coordination sphere of the complex; 2) the stretching carbonyl band at 1700 cm^{-1} is shifted to lower wave numbers relative to that of the free ligand indicating the participation of the carbonyl group in chelation; 3) the CH bending vibration band of the $-CH_2CO-$ moiety had disappeared, while a new band at 1028 cm^{-1} is seen which is assigned to the enolic $\nu(C-O)$ as a result of enolization followed by complexation. Therefore, the structure in Fig. 3 may be assigned to $[Cu_2L^e(OH)(H_2O)_2]$.



	X	Y	Y'
H_2L^a :	*p*-OCH_3	$(CH_3)_2CO$	H_2O
H_2L^b :	*p*-CH_3	H_2O	H_2O
H_2L^c :	*p*-Br	$(CH_3)_2CO$	$(CH_3)_2CO$
H_2L^d :	*p*-Cl	$(CH_3)_2CO$	$(CH_3)_2CO$

Fig. 2. Suggested Structure of the Complexes Cu(II)-$H_2L^{a\text{-}d}$

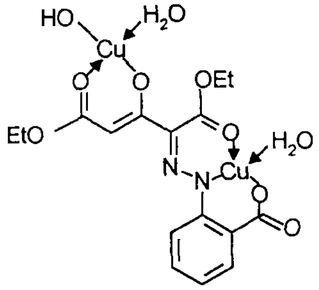
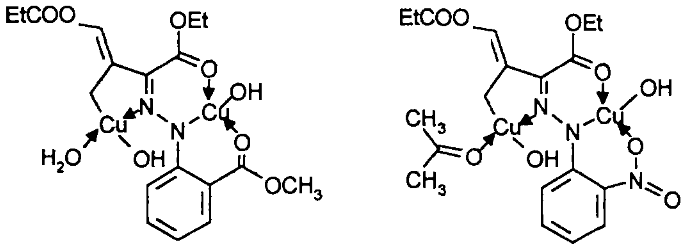


Fig. 3. Suggested Structure of $[Cu_2L^e(OH)(H_2O)_2]$

On the other hand, the *o*-methyl ester (H_2L^f) and *o*-nitro (H_2L^g) ligand derivatives behave as dinuclear, dibasic, pentadentate ligands coordinating via the enolic OH and C=N groups of the hydrazone moiety on one side and NH, CO (ester group 1) and CO (ester attached to the aromatic ring) or NO (of the nitro group), respectively, on the other side. This behavior is revealed by 1) the appearance of a broad medium band at 3000-3600 cm^{-1} which may be assigned to ν(OH) of OH ions and H_2O molecules that complete the coordination sphere of the complexes; 2) the appearance of ν(C=O) bands at 1729 and 1720 cm^{-1} for $[Cu_2L^f(OH)_2(H_2O)]$ and $[Cu_2L^g(OH)_2(CH_3)_2CO]$, respectively, which are almost at the same positions as those of their corresponding ligands, confirming the exclusion of the ester group 2 from the complexation process, in contrast to that reported for the Cu(II) complexes of H_2L^{a-e} and, consequently, they coordinated with Cu(II) ions through the C=N moiety; 3) the disappearance of the δ(CH) band of the $-CH_2CO-$ moiety from the spectra of the complexes and a new band at 1035 cm^{-1} which may be assigned to enolic ν(C-O), thus confirming the chelation through the enolic OH. The structures of the $[Cu_2L^f(OH)_2(H_2O)]$ and $[Cu_2L^g(OH)_2(CH_3)_2CO]$ complexes may be represented as shown in Fig. 4.

On trying to prepare 1:1 (M:L) complexes by adjusting the time of current flow, the separated products did not give the expected stoichiometric ratio, except H_2L^h, which formed the complex $[CuL^h(H_2O)(CH_3)_2CO]$ as revealed by the elemental analyses (Table I). The ligand behaves as bidentate dibasic acid via NH and OH (enolic). The structure of the $[CuL^h(H_2O)(CH_3)_2CO]$ complex was confirmed by its IR spectrum by the following observations: 1) the appearance of bands at 3432, 1270 and 695 cm^{-1} which may be assigned to ν(OH), δ(OH) and ρ_r(OH) of the coordinated water molecule; 2) the shift of ν(C=O) to lower wave number as a single band at 1700 cm^{-1} which may be assigned to the two conjugated ester groups indicating the participation of the carbonyl group in chelation through its enolized form. The proposed structure of the $[CuL^h(H_2O)(CH_3)_2CO]$ complex may be as shown in Fig. 5.

A dimer complex (mole ratio 2:2)[16], $[Cu_2L^i_2]$, was formed upon chelation of the *o*-hydroxy derivative H_3L^i by adjusting the time of anodic



$[Cu_2L^f(OH)_2(H_2O)]$ $[Cu_2L^g(OH)_2(CH_3)_2CO]$

Fig. 4. Suggested Structures of the Complexes of the Ligands H_2L^f and H_2L^g

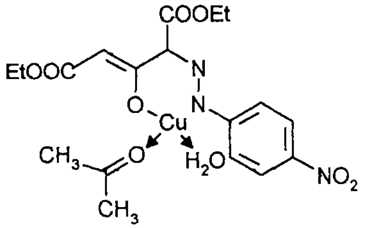


Fig. 5. Suggested Structure of $[CuL^h(H_2O)(CH_3)_2CO]$

dissolution trying to prepare a 1:1 complex. This assumption was revealed from the IR spectrum of the $[Cu_2L^i_2]$ which displayed: 1) no band for the OH group indicating the participation of phenolic OH in the chelation and the exclusion of water molecules from the coordination sphere; 2) the ν(NH) band was not observed indicating its participation in complexation; 3) bands at 1732 and 1693 cm^{-1} are assigned to ν(C=O), the first band attributed to the ester group 1 has remained unaltered, while the second band is shifted to lower wave number due to the participation of the ester group 2 in the coordination process. These results indicate that H_3L^i behaves as a dinuclear, dibasic, tetradentate ligand coordinating via OH (phenolic) and NH on one side and the

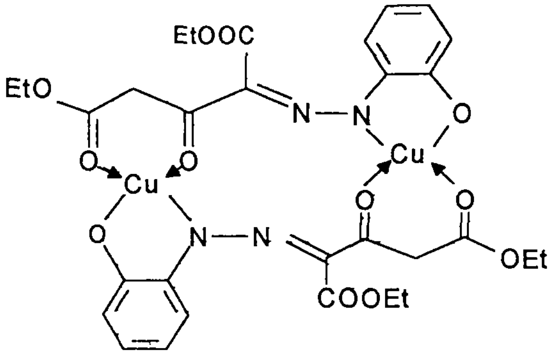


Fig. 6. Suggested Structure of $[Cu_2L^i{}_2]$

coordination sphere is completed by the ketonic and ester carbonyls as shown in Fig. 6.

By controlling the time of current flow, the *p*-chloro ligand derivative H_2L^d formed a complex of the formula $[Cu(HL^d)_2]$. The ligand behaves as a bidentate, monobasic acid coordinating via the β-keto ester moiety in a well-established form of complexation. The structure of this complex is proposed based on the IR spectrum which showed a weak ν(NH) band at 3210 cm^{-1} indicating its exclusion from the chelation and a shift to lower wave number of the ν(C=O) band to 1706 cm^{-1}, assigned to the free conjugated ester moiety (ester group 1) that is hydrogen-bonded to the NH proton. The other carbonyl bands (ketonic, ester group 2) are not observed due to their participation in complexation (Fig. 7).

All compounds show Cu-N[17] and Cu-O[18] stretching vibrational bands at 469-509 cm^{-1} and 434 cm^{-1}, respectively, except $Cu(HL^d)_2$ which shows only a Cu-O band.

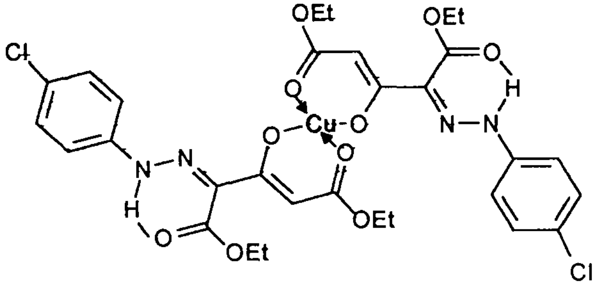


Fig. 7. Suggested Structure of [Cu(HL^d)$_2$]

Thermogravimetric Analysis

TG curves of the Cu(II) complexes show no mass loss below 150° C reflecting the absence of hydrated water molecules in these complexes as indicated from the elemental analyses results. The TG data are collected in Table III.

The final combustion residue of the [$Cu_2L^a(OH)_2H_2O(CH_3)_2CO$], [$Cu_2L^c(OH)_2((CH_3)_2CO)_2$], [Cu(HL^d)$_2$], [$Cu_2L^g(OH)_2(CH_3)_2CO$] (2:1) and [$CuL^h(H_2O)(CH_3)_2CO$] (1:1) complexes at 450-650° C indicate the formation of the oxide Cu_2O.

The complexes [$Cu_2L^b(OH)_2(H_2O)_2$], [$Cu_2L^e(OH)(H_2O)_2$] and [$Cu_2L^f(OH)_2(H_2O)$] start losing water around 165-190° C with a weight-loss corresponding to the loss of the water molecules associated with an endothermic peak in the DTA curves. The decomposition proceeds slowly and the final residue at about 340-355° C corresponds to the formation of Cu_2O_3 which is associated with an exothermic peak in the DTA curve in the same temperature range.

The TGA data of the complexes [Cu(HL^d)$_2$] and [$Cu_2L^i{}_2$] show an inflection point accompanied by about 50% weight loss in the temperature

Table III. Thermogravimetric Analysis (TGA) of the Cu(II) Complexes of Diethyl 2,3-Dioxopentanedioate-2-arylhydrazone Derivatives.

Formula	Temp. °C	Weight loss (%)		Assignment[a]
		Calcd.	Found	
$[Cu_2L^a(OH)_2H_2O(CH_3)_2CO]$	450	25.04	22.76	Cu_2O
$[Cu_2L^b(OH)_2(H_2O)_2]$	190	6.99	8.00	H_2O
	340	36.31	34.23	Cu_2O_3
$[Cu_2L^c(OH)_2((CH_3)_2CO)_2]$	170-300		54.70	unstable intermediate
	650	21.67	19.99	Cu_2O
$[Cu_2L^d(OH)_2((CH_3)_2CO)_2]$	150-325		49.12	unstable intermediate
	640	23.23	22.24	Cu_2O
$[Cu(HL^d)_2]$	180-330		59.60	unstable intermediate
	590	10.70	10.30	CuO
$[Cu_2L^e(OH)(H_2O)_2]$	200	6.83	7.00	H_2O
	342	35.46	35.26	Cu_2O_3
$[Cu_2L^f(OH)_2(H_2O)]$	165	3.33	3.00	H_2O
	355	34.54	33.04	Cu_2O_3
$[Cu_2L^g(OH)_2(CH_3)_2CO]$	200-300		44.70	unstable intermediate
	500	25.18	26.67	Cu_2O
$[CuL^h(H_2O)(CH_3)_2CO]$	450	14.64	12.05	Cu_2O
$[Cu_2L^i_2]$	240-350			unstable intermediate
	460	20.72	20.03	2CuO

[a] Various copper oxides were identified from the percentage of the final combustion residue.

range 300-350° C due to formation of unstable intermediates. The complete combustion to the final residue, 20.03 and 10.30%, at about 460 and 590° C corresponds to the formation of CuO (theoretical values, 20.72 and 10.70%, respectively).

It is worth mentioning that the thermal decomposition of the complexes, which contain an acetone molecule in their coordination spheres, led to the formation of Cu_2O. Complexes that containing water molecules led to the formation of Cu_2O_3 and the complexes that contain neither acetone nor water gave in their thermal decomposition CuO. The various copper oxides were identified from the percentage of the final combustion residue.

Electronic Spectra and Magnetic Moments

The electronic spectra of the Cu(II) complexes showed bands at 19146-21978 cm^{-1} and/or 24612-27203 cm^{-1} which emphasize the square-planar structure of these complexes[19]. The appearance of a high-energy band at 32123-34014 cm^{-1} may be assigned to charge transfer through the new electronic structure of the formed complexes[20].

Several studies show a very low magnetic moment for dinuclear complexes with bridging groups suggesting a partial spin-pairing between copper(II) ions[8]. The relatively low magnetic moments, 1.27-1.61 B.M. per copper ion for the copper complexes of H_2L^{a-g} (2:1) and $[Cu_2L^i_2]$ (2:2), may be interpreted by considering weak interactions between the two copper(II) ions. The magnetic moment values of the $[CuL^h(H_2O)(CH_3)_2CO]$ (1:1) and $[Cu(HL^d)_2]$ (1:2) complexes are 1.82 and 1.87 B.M., respectively, which are in good agreement with those reported for a spin-only unpaired electron[21].

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