Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

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To cite this article: Y. M. Issa & W. H. Hegazy (2000): Preparation and Characterization of Some Substituted 3-benzylidene-2,4-pentanediones and Some of Their Metal Complexes, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 30:9, 1731-1746

To link to this article: http://dx.doi.org/10.1080/00945710009351865

SYNTH. REACT. INORG. MET.-ORG. CHEM., 30(9), 1731-1746 (2000)

PREPARATION AND CHARACTERIZATION OF SOME SUBSTITUTED 3-BENZYLIDENE-2,4-PENTANEDIONES AND SOME OF THEIR METAL COMPLEXES

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ABSTRACT

Several substituted 3-benzyledine-2,4-pentanediones have been prepared, purified and recrystallized from ethanol till constant melting points. The resulting compounds have been characterized by elemental analyses, IR, ^{1}H NMR and mass spectroscopy. Metal complexes of the title ligands were prepared and characterized by elemental analyses, IR spectroscopy, magnetic susceptibility and thermogravimetry. The analytical, spectroscopic and magnetic moment data are in accordance with the suggested formulae.

INTRODUCTION

β-Diketones, especially acetylacetone, are known to coordinate, as ligands, with many metal ions[1]. In the majority of cases, the diketone ligand binds to the metal ion through its anionic enol form and the pseudo aromaticity persists in the metal chelates. Infrared spectra demonstrating hydrogen bonding in the enol form of β-diketones have been reported[2]. Complex formation is conceived by replacement of

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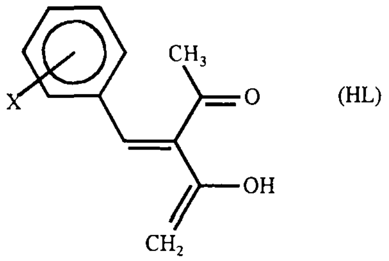
the enolic proton by the metal ion, commonly in a bidentate fashion. Condensation of β-diketones with aldehydes was first carried out by Knövenagel and Arnot[3] to prepare 3-arylidene-2,4-pentanediones, and many Knövenagel condensates in a high yield and pure form have also been reported[4-7]. The effect of substituents on these ligands in position 3 on the tautomeric equilibria has been investigated by NMR spectroscopy[8]. Also, substituent effects on infrared spectra, ^{13}C and ^{1}H chemical shifts of some 3-benzylidene-2,4-pentanediones have been studied[9,10]. 3-Arylidene-2,4-pentanediones and related compounds are used as chelating agents with many transition metals[11-14]. The photochromic behavior[15] of β-diketone compounds, the extractive separation and spectrophotometric determination of vanadium(III)[16,17] with benzoylacetone and pH-potentiometric determination of the stability of Cu(II)-β-diketonato mixed-ligand complexes[18] were also studied.

Recently, the Knövenagel condensation of substituted benzylidenes with active methylene compounds was performed very efficiently by using ultra-stable Y Zeolite as a heterogeneous catalyst[19]

The aim of this article is to elicit the optimum conditions to prepare (in very high purity grade) some Knövenagel condensates and their metal complexes with some transition metals and to characterize these compounds by elemental analyses, thermogravimetry, magnetic susceptibility, IR, NMR and mass spectroscopy. Figure 1 represents the structure of the ligands.

EXPERIMENTAL

The following chemicals were used without further purification: Acetylacetone, benzaldehyde, *o*-salicylaldehyde, *o*-chlorobenzaldehyde and *o*-anisaldehyde (Merck, Germany); *m*-anisaldehyde, *p*-flourobenzaldehyde, *p*-bromobenzaldehyde (Riedel de Haen AG, Germany), *p*-$(CH_3)_2N$-benzaldehyde, *p*-chlorobenzaldehyde, $Cu(CH_3COO)_2.H_2O$, $CoCl_2.2H_2O$ and $NiCl_2.6H_2O$ (B.D.H., England). Absolute ethanol was completely dried *via* reflux over calcium oxide for more than 6 h. Benzene, acetone and petroleum ether (40-60° C) were of >99% purity. Elemental analyses were performed at the Microanalytical Center, Cairo University, Egypt. Melting points were recorded on a Gallenkamp melting point



X = H (HL^1), *p*-Cl (HL^2), *p*-Br (HL^3), *p*-F (HL^4), *p*-OCH_3 (HL^5), *o*-OH (HL^6), *o*-Cl (HL^7), *m*-OCH_3 (HL^8) and *p*-$(CH_3)_2N$ (HL^9)

Fig. 1. The Structure of the Ligands.

apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 infrared spectrophotometer using KBr disks. ^{1}H NMR spectra were recorded using a Varian EM 390-90 MHz NMR spectrometer in DMSO-d_6 with TMS as internal reference. Mass spectra were recorded with the aid of a GCMS-QP 1000 EX Shimadzu mass spectrometer at 70 eV using a direct insertion probe at temperatures of 25-300° C. Thermogravimetric analyses were performed under a N_2 atmosphere using a Shimadzu TGA-50H with a flow rate of 30 mL/min. The magnetic susceptibilities were measured using a Sherwood Scientific Ltd. magnetic susceptibility balance (England).

Preparation of the Ligands

Condensation of acetylacetone with substituted benzaldehydes was performed by heating equimolar amounts (0.05 mole) under reflux in 50 mL ethanol in the presence of 5 drops of piperidine as a catalyst for not less than 10 h (until the solution turns dark brown). The solution was then cooled and the condensed product was separated by adding 3 mL benzene and 20 mL petroleum ether (40-60° C). The Knövenagel condensate (HL) was isolated by filtration, washed and recrystallized from ethanol to constant melting point. The colors, melting points, % yields and elemental analyses are given in Table I.

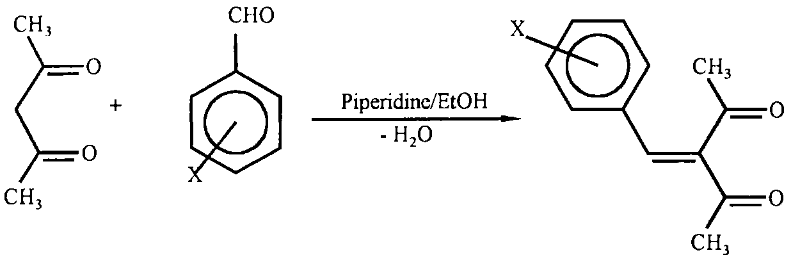
Preparation of the Complexes

The metal complexes were prepared by the following general procedure for the ligand HL[1] with Co(II), Ni(II) and Cu(II), and the ligands HL[2], HL[4], HL[5] and HL[6] with Cu(II): A solution containing 3 mmol of the ligand in 30 mL of ethanol was added to a solution of 5 mmol of $CoCl_2.2H_2O$, $NiCl_2.6H_2O$ or $Cu(CH_3COO)_2.H_2O$. The mixtures were refluxed for 6 h, cooled to room temperature and concentrated to 10 mL by evaporating the solvent. The complexes were then isolated by filtration, extensively washed with doubly distilled water, recrystallized from acetone and air-dried.

RESULTS AND DISCUSSION

The Ligands

The Knövenagel condensates (HL) were prepared *via* condensation of 0.05 mole acetylacetone (β-diketone) and 0.05 mole aldehyde in the presence of piperidine as a catalyst according to eq.(1).



(1)

The resulting compounds were characterized by elemental analyses (Table I); IR spectral data (Table II); ^1H NMR spectral data (Table III) and mass spectral data (Table IV). The elemental analyses were found to be in agreement with the calculated data.

The infrared spectra of the ligands show broad and strong bands in the region 3431-3401 cm^{-1} assigned to OH stretching vibrations for the ligands HL[1] to HL[5], HL[8] and HL[9] which may be due to enolization of the acetyl group (CH_3-C=O). The ligand

Table I. Physical Properties and Elemental Analyses of the Ligands.

Ligand (Formula Weights)		Color	Yield, %	M.p., °C	Elemental Analyses Found (Calculated)	
					% C	% H
HL^1	$C_{12}H_{12}O_2$ (188.225)	White	72	173°	69.73 (69.90)	6.90 (6.80)
HL^2	$C_{12}H_{11}O_2Cl$ (222.67)	Lemon-Yellow	79	237°	64.93 (64.40)	5.00 (5.37)
HL^3	$C_{12}H_{11}O_2Br$ (267.121)	Orange	81	163°	54.30 (53.90)	3.80 (4.12)
HL^4	$C_{12}H_{11}O_2F.H_2O$ (224.215)	Yellow	62	166°	64.60 (64.29)	6.10 (5.99)
HL^5	$C_{13}H_{14}O_3.H_2O$ (236.251)	White	85	241°	66.50 (66.30)	5.40 (5.90)
HL^6	$C_{12}H_{12}O_3$ (204.224)	Yellow	59	115°	70.60 (70.60)	5.70 (5.88)
HL^7	$C_{12}H_{11}O_2Cl$ (222.67)	Orange	63	147°	64.80 (64.40)	5.12 (5.37)
HL^8	$C_{13}H_{14}O_3.H_2O$ (236.251)	Orange	76	243°	66.40 (66.10)	5.88 (5.90)
HL^9	$C_{14}H_{18}O_2N.H_2O$ (250.301)	Orange	57	224°	67.60 (67.74)	6.80 (7.26)

HL^6 shows a broad band at 2993 cm^{-1} due to the presence of a phenolic OH group. Weak bands in the region 2980-2905 cm^{-1} are assigned to CH_3 stretching vibrations. The ligands also show two sharp strong bands in the regions 1718-1700 cm^{-1} and 1697-1693 cm^{-1} are assigned to the stretching vibrations of the two carbonyl groups. The two bands at *ca.* 1600 and 1500 cm^{-1} correspond to C=C ring stretching. Bands in the region 1375-1360 cm^{-1} are assigned to in-plane bending vibrations of the methyl groups. The out-of-plane bending vibrations of the ring CH bonds are observed in the 781-727 cm^{-1} region.

The ^1H NMR chemical shifts and coupling constants of the 3-benzylidene-2,4-pentanediones in DMSO-d_6 are given in Table III, suggesting two tautomeric forms, the α-form and the β-form, arising from keto-enol tautomerism, as shown in eq.(2).

Table II. Infrared Bands of the Ligands (in cm^{-1}).

HL^1	HL^2	HL^3	HL^4	HL^5	HL^6	HL^8	HL^9	Band Assignments
3431 s	3411 s	3412 s	3401 s	3411 s	2993 vb	3414 m	3421 m	ν(OH)
2980 w	2974 w	2974 w	2974 w	2971 w	2972 w	2926 w	2971 w	ν(CH_3)
1718 s	1718 s	1718 s	1717 s	1718 s	1700 s	1717 s	1718 s	ν(C=O)
1693 s	1697 s	1695 s	1697 s	1693 s	1668 s	1694 s	1693 s	ν(C=O)
1600 w	1614 w	1602 w	1603 w	1612 m	1604 s	1594 s	1601 s	ν(C=C)
1499 m	1495 m	1491 m	1513 m	1516 s	1485 m	1492 m	1527 m	ν(C=C)
1361 m	1365 m	1364 m	1360 s	1364 s	1375 s	1362 m	1372 s	δ(CH_3)
765 s	731 m	748 m	763 m	759 m	756 s	781 s	727 m	Out-of-plane γ(C-H)

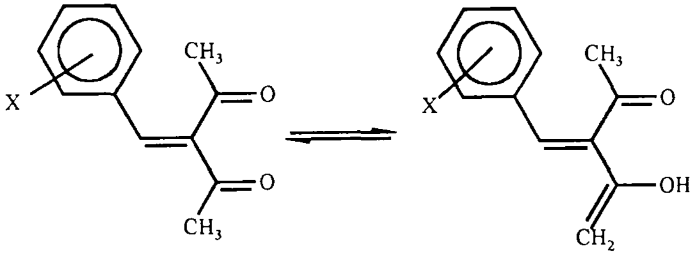
Table III. ^{1}H NMR Spectroscopic Data of the Ligands.

Ligands	(s, 3H) β–Form δ(ppm)	(s, 6H) α–Form δ(ppm)	(d, 1H) diasterotropic CH$_2$ group of β–Form δ(ppm) (J)(Hz)	(d, 1H) diasterotropic CH$_2$ group of β–Form δ(ppm) (J)(Hz)	(s, 3H) methoxy group attached to the ring δ(ppm)	(dd, 2H) of 2 CH groups of α- and β-forms δ(ppm) (J)(Hz)	(s, 1H) of OH group of β–Forms (exchangable) δ(ppm)	(m, arom. H) δ(ppm)
HL^1	1.20	1.99	2.37 (6.21)	2.95 (6.21)	--	4.10 (5.40)	5.20	7.10-7.40
HL^2	1.20	1.98	2.36 (6.12)	2.94 (6.12)	--	4.08 (5.32)	5.27	7.20-7.50
HL^3	1.19	1.94	2.36 (6.03)	2.90 (6.03)	--	4.20 (5.56)	5.15	7.25 (d, 2H) 7.50 (d, 2H) J = 3.78
HL^4	1.20	1.93	2.37 (6.21)	2.94 (6.21)	--	4.15 (5.49)	5.22	7.10-7.50
HL^5	1.19	1.92	2.32 (6.12)	2.93 (6.12)	3.75	4.10 (5.41)	5.19	6.83 (d, 2H) 7.25 (d, 2H) J = 3.87
HL^6	δ 1.82 ppm (s, 3 H) the first methyl group. δ 2.43 ppm (s, 3 H) the second methyl group. δ 3.84 ppm (s, 1 H) the phenolic OH (exchangeable). δ 7.20 ppm (m, 4 arom .H). δ 7.80 ppm (s, 1 H) ethylenic (CH) group.							

Table IV. m/z Values (Relative Abundances) of the Principal Fragments in The Mass Spectra of the Ligands.

Ligand	$[M]^{\cdot}$	[A]	[B]	[C]	[D]
HL^1	188 (21)	173 (3.5)	131 (26)	103 (21)	77 (27.6)
HL^2	222 (-)	207 (-)	165 (4)	137 (44)	111 (54.6)
HL^3	267 (13)	252 (3.5)	210 (19)	182 (13)	157 (4.8)
HL^4	206 (16.7)	191 (2.6)	149 (23)	121 (9.5)	96 (3.0)
HL^5	218 (18.2)	203 (8)	161 (28)	133 (21)	108 (6.2)
HL^6	205 (4)	190 (5.5)	148 (1)	120 (1.5)	94 (1)

HL^1: M – 3 = 185 (100)
HL^3: M – 2 = 265 (100)
HL^4: M – 3 = 203 (100)
HL^5: M – 3 = 215 (100)



α- form β - form

(2)

The spectroscopic data support the existence of this equilibrium in several ways.

It is clear from the data in Table III that there are two chemical shifts (s, 3H) for the β-form and (s, 6H) for the α-form of the two methyl groups which support the enolization process. It was found that for HL^6, there is only one form (keto form) of the condensate and no enolization is observed. Also, the IR spectra show a very broad band at 2993 cm ^{1} for HL^6 which is due to a hydrogen bonded but not a free OH group.

The mass spectrometic fragmentation pattern of the ligands is shown in Fig. 2. The molecular ions in the mass spectra and their relative abundances are shown in Table IV. It is notable that the first fragmentation occured by elimination of only one methyl group since the two methyl groups are not equivalent due to enolization of the second one.

The Complexes

Reactions of the ligand HL^1 with Co(II), Ni(II) and Cu(II) salts and ligands HL^2, HL^4, HL^5 and HL^6 with Cu(II) acetate were performed in neutral solution to give the ionic complexes $[Co(L^1)(H_2O)_4]Cl$, $[Ni(L^1)(H_2O)_4]Cl.H_2O$, $[Cu(L^1)(H_2O)_4]$-$AcO.H_2O$, $[Cu(L^5)(H_2O)_4]AcO.H_2O$, $[Cu(L^6)(H_2O)_4](AcO)_2.H_2O$ and the neutral complexes $[Cu(L^2)_2(H_2O)_2]2H_2O$ and $[Cu(L^4)_2(H_2O)_2]H_2O$. The physical properties, magnetic moments and elemental analyses of the complexes are listed in Table V. The ligand coordination sites involved in bonding with the metal ions have been determined by careful comparison of the infrared absorption bands of the complexes (Table VI), with those of the parent ligands. The relevant changes were the following; a shift to lower frequency (13-20 cm^{-1}) in the higher energy carbonyl vibration while the lower energy vibration is very weak and shifts to lower frequency (39-63 cm^{-1}) or even disappears; shifts to lower frequencies (10-33 cm^{-1}) in the C-C stretching of the methyl group in-plane bending vibrations. All these shifts suggest coordination of the ligand as an enolate. The 3550-3000 cm^{-1} region of the spectra of all complexes shows broad bands, which may be due to lattice and/or coordinated water molecules associated with the complexes. Therefore, it is difficult to draw conclusions based on the bands appearing in this region. Elemental analyses, Table V, as well as thermogravimetry of the complexes, Table VII, suggest the presence of associated water molecules for each complex.

The thermogravimetric analyses of the metal complexes were measured from ambient temperature up to 800° C at a heating rate of 10° C min^{-1}. The results are collected in Table VII and were used in the calculation of lattice water molecules,

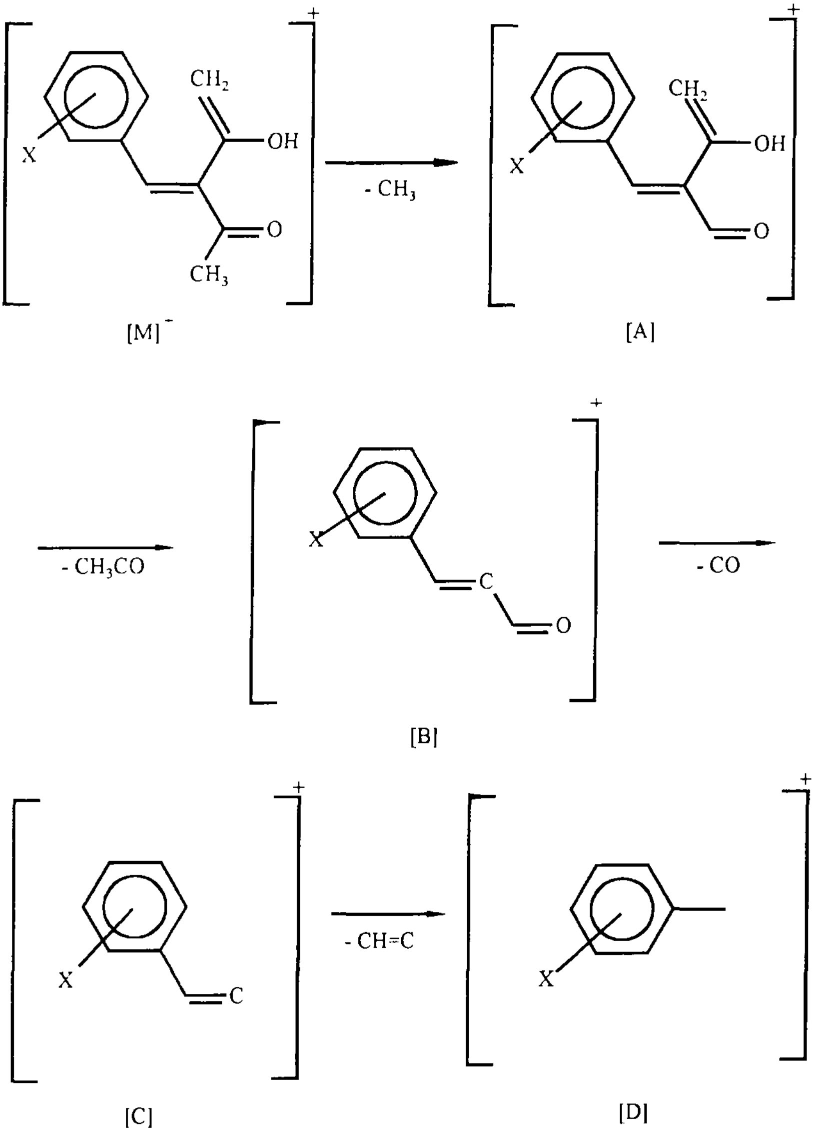


Fig.2. The General Mass Spectral Fragmentation Pattern of the Ligands.

Table V. Analyses of the Complexes.

Complex	Color	M.p., °C	Yield, %	μ_{eff} (B.M.) Calc.	μ_{eff} (B.M.) Found	Elemental Analyses Found (Calc.)		
						% C	% H	Cl^-
$[Co(L^1)(H_2O)_4]Cl$	Brown	> 300°	62	3.87	4.12	40.17 (40.73)	5.60 (5.38)	10.33 (10.04)
$[Ni(L^1)(H_2O)_4]Cl.H_2O$	Gray	> 300°	65	2.83	2.97	39.11 (38.79)	5.20 (5.65)	8.80 (9.56)
$[Cu(L^1)(H_2O)_4]AcO.H_2O$	Green	> 300°	70	1.73	1.84	39.65 (39.05)	5.80 (6.00)	--
$[Cu(L^2)_2(H_2O)_2]2H_2O$	Green	> 300°	72	1.73	1.90	59.55 (59.78)	4.80 (4.84)	--
$[Cu(L^4)_2(H_2O)_2]H_2O$	Green	> 300°	69	1.73	1.93	55.00 (54.60)	5.10 (4.93)	--
$[Ni(L^4)_2(H_2O)_2]H_2O$	Gray	> 300°	66	2.83	3.05	55.40 (55.10)	5.00 (4.98)	--
$[Cu(L^5)(H_2O)_4]AcO.H_2O$	Green	> 300°	65	1.73	1.81	38.72 (39.12)	6.11 (6.05)	--
$[Cu(L^6)(H_2O)_4](AcO)_2.H_2O$	Green	> 300°	59	1.73	1.70	40.00 (40.38)	5.78 (5.89)	--

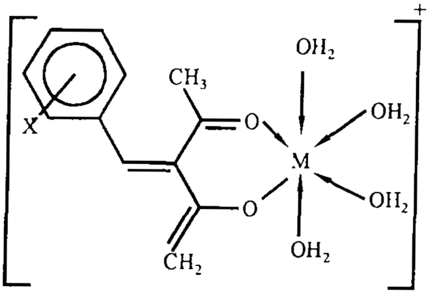
Table VI. Characteristic IR Bands of Complexes (cm^{-1}).

HL^1 : Co 1 : 1	HL^1: Ni 1 : 1	HL^1 : Cu 1 : 1	HL^2 : Cu 2 : 1	HL^4 : Cu 2 : 1	HL^4 : Ni 2 : 1	HL^5 : Cu 1 : 1	HL^6 : Cu 1 : 1	Band Assignments
3550 s	3200 b	3523 s	3200 vb	3525 s	3200 vb	3523 m	2999 vb	ν(OH)
1697 m	1705 s	1701 m	1705 m	1707 s	1701 m	1701 m	1668 s	ν(C=O)
1625 w	1650 w	1654 w	--	--	--	--	1627 s	ν(C=O)
1560 s	1585 s	1572 s	1570 s	1569 s	1577 s	1573 s	1604 m	ν(C=C)
1491 w	1492 m	1491 w	1489 m	1508 s	1508 s	1512 s	1485 m	ν(C=C)
1359 m	1358 m	1348 s	1352 m	1350 s	1360 s	1348 s	1375 s	δ(C–H) (CH_3)

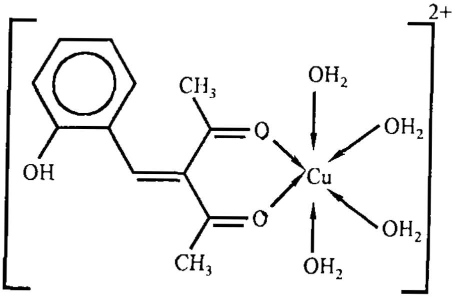
Table VII. Thermogravimetric Analyses of the Solid Complexes.

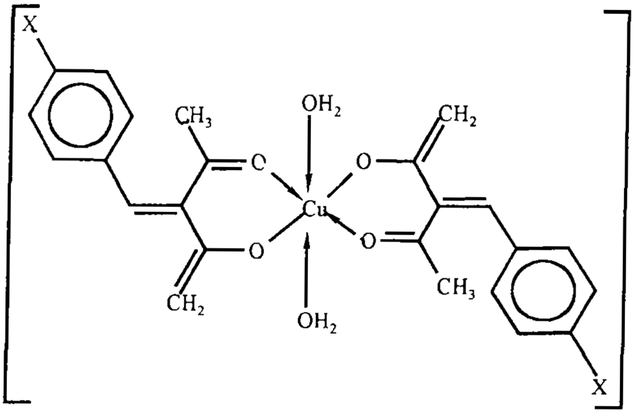
Complex	Lattice Water				Coordinated Water				% of Metal	
	Temp., °C Up to	Wt. Loss %		No. of Water Molecules	Temp. Range, °C	Wt. Loss %		No. of Water Molecules	Calc.	Found
		Calc.	Found			Calc.	Found			
$[Co(C_{12}H_{12}O_2)(H_2O)_4]$	--	--	--	--	150–260	22.57	22.22	4	16.70	17.80
$[Ni(C_{12}H_{12}O_2)(H_2O)_4].H_2O$	100	5.35	5.10	1	160-230	21.38	24.14	4	15.80	15.86
$[Cu(C_{12}H_{12}O_2)(H_2O)_4]H_2O$	100	5.27	4.29	1	190-250	21.00[a]	43.00	4[a]	15.90	16.10
$[Cu(C_{12}H_{11}O_2Cl)_2(H_2O)_2]2H_2O$	120	6.21	6.59	2	200-265	6.20[a]	60.00	2[a]	10.98	9.90
$[Cu(C_{12}H_{11}O_2F)_2(H_2O)_2]H_2O$	115	3.40	4.00	1	185-260	6.80[a]	55.00	2[a]	12.04	12.67
$[Cu(C_{13}H_{14}O_3)(H_2O)_4]H_2O$	135	5.06	5.07	1	180-230	20.25[a]	60.00	4[a]	14.78	14.03
$[Cu(C_{12}H_{12}O_3)(H_2O)_4]H_2O$	120	5.03	5.46	1	180-220	22.14	23.04	4	13.35	13.41

[a] These values are not assured since another weight loss occurred at the temperature range of the coordinated water loss.



X = H and *p*-OCH$_3$





X = *p*-Cl and *p*-F

Fig. 3. Structural Formulae of the Complexes.

coordinated water molecules and metal percent. It is apparent that the coordinated water molecules are 4 in the 1:1 complexes while they are 2 in the case of the 1:2 complexes, which is in concert with the data in Table VI, and the percent of the metals and the proposed structures. The results obtained are in good agreement with the theoretical ones.

The thermograms of the complexes show the removal of lattice water molecules starting from 85 up to 135° C. The anhydrous complex $[Co(C_{12}H_{12}O_2)(H_2O)_4]Cl$ shows thermal stability up to 150° C. The removal of coordinated water molecules from the complexes takes place within the temperature range 150-265° C. It is notable that for $[Cu(L^1)(H_2O)_4](AcO)H_2O$, $[Cu(L^2)_2(H_2O)_2]2H_2O$, $[Cu(L^4)_2(H_2O)_2]H_2O$ and $[Cu(L^5)(H_2O)_4]AcO.H_2O$ another weight loss occurred in the temperature range of coordinated water loss, but the postulated formulae are in convention with the elemental analyses of carbon, hydrogen and % of metal residue. The decomposition of the complexes to metal oxides takes place within the temperature range 475 to 730° C.

The magnetic moment of the $[Co(C_{12}H_{12}O_2)(H_2O)_4]Cl$ complex indicates the presence of three unpaired electrons which suggests an octahedral geometry with a weak ligand field; the magnetic moments of $[Ni(C_{12}H_{12}O_2)(H_2O)_4]Cl.H_2O$ and $[Ni(L^4)_2(H_2O)_2]H_2O$ indicate the presence of two unpaired electrons, thus suggesting, together with the data given in Table VII, octahedral geometries; while the magnetic moments of Cu(II) complexes indicate the presence of one unpaired electron in each complex which suggest distorted octahedral geometries. All magnetic moment data are listed in Table V. From the data given in Tables V, VI and VII, the suggested structural formulae of the complexes may be represented as shown in Fig. 3.

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Received: 5 January 2000
Accepted: 23 June 2000

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