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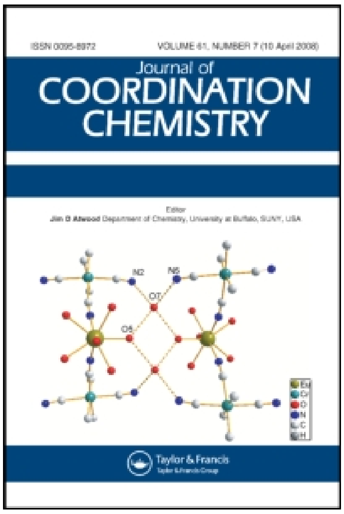

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopy and thermal analysis of copper(II) hydrazone complexes

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To cite this Article Al-Hazmi, Gamil A. and El-Asmy, Ahmed A.(2009) 'Synthesis, spectroscopy and thermal analysis of copper(II) hydrazone complexes', Journal of Coordination Chemistry, 62: 2, 337 — 345
To link to this Article: DOI: 10.1080/00958970802226411
URL: http://dx.doi.org/10.1080/00958970802226411

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Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 337–345

Synthesis, spectroscopy and thermal analysis of copper(II) hydrazone complexes

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(*Received 3 March 2008; in final form 31 March 2008*)

The chelating behavior of some hydrazones towards Cu(II) has been investigated. The isolated complexes were characterized by elemental analysis, magnetic moment, spectra (electronic, IR and ms) and thermal measurements. The IR spectra showed that the ligands are deprotonated in the complexes as bidentate, tridentate and binegative tridentate. Protonation constants of the ligands and the stability constants of their Cu(II) complexes were calculated. Square-planar, square-pyramidal, tetrahedral and/or distorted octahedral structures are proposed. The TGA data help to confirm the chemical formula of the complexes and indicated the steps of their thermal degradations.

Keywords: Cu(II) complexes; Hydrazones; Spectra

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1. Introduction

Hydrazones of the azomethine class are distinguished from imines or oximes by two adjacent N atoms. Hydrazones have a variety of applications such as hole transporting agents [1] in organic layer photo conductors, as drugs for treatment of cancer, schizophrenia, leprosy, etc. [2–6] and in synthetic and industrial chemistry [7]. Hydrazones have strong tendency to chelate transition metals [8–12].

Hydrazides and hydrazones have several coordination sites and can coordinate to transition metals either in the enol (I) or keto form (II) [13–15], as shown in figure 1.

In this article, the synthesis, characterization, thermal and spectroscopic studies of Cu(II) complexes are reported.

2. Experimental

All chemicals used were analytical reagents (BDH or Merck grades) and used as supplied. The formula, abbreviations and names of the ligands are listed in table 1.

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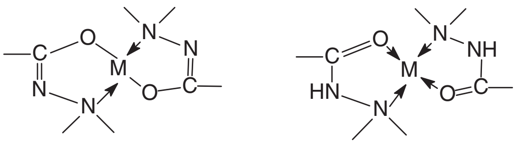
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802226411



(I) (II)

Figure 1. Enol(I) and keto(II) forms of hydrazone complexes.

Table 1. Abbreviations, names, melting points, elemental analyses and formula weights (F.W.) of the ligands.

				Found (Calcd) (%)		F. W	
Abbreviation	Full name	Color	M.P. (°C)	C	H	Found*	Calcd
HCFH	1-Cyanoacyl-3-furfuraldehyde-2-hydrazone	Light yellow	160	54.8(54.2)	3.6(3.9)	–	177.1
HCBH	1-Cyanoacyl-3-benzaldehyde-2-hydrazone	White	155	63.3(64.1)	4.8(4.8)	188.0	187.2
H_2CSH	1-Cyanoacyl-3-salicylaldehyde-2-hydrazone	Yellow	190	59.3(59.1)	4.9(4.5)	–	203.2
HCAH	1-Cyanoacyl-3-acetylacetone-2-hydrazone	White	170	53.6(53.0)	5.8(6.1)	180.0	181.2
HCphH	1-Cyanoacyl-3-acetophenone-2-hydrazone	White	120	65.4(65.7)	5.2(5.5)	202.0	201.2
HCNH	1-Cyanoacyl-3-crotonaldehyde-2-hydrazone	Yellowish white	135	56.2(55.6)	5.7(6.0)	–	151.2
HCMH	1-Cyanoacyl-3-cinnamaldehyde-2-hydrazone	Yellow	168	68.0(67.6)	4.8(5.2)	213.0	213.2

*Values obtained from mass spectra.

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2.1. *Synthesis of the ligands*

2.1.1. Synthesis of cyanoacylhydrazine. Cyanoacylhydrazine was prepared as reported earlier [6] by mixing 22.6 mL (0.2 mol) of ethyl cyanoacetate, dissolved in 20 mL ethanol, with 25 mL (0.05 mol) of hydrazine hydrate. The mixture was allowed to cool for 4 h, the white precipitate was filtered off, washed with 5 mL absolute ethanol and recrystallized from absolute ethanol.

2.1.2. Synthesis of hydrazone derivatives. The hydrazones (figure 2) were prepared by condensation of 1 : 1 molar ratio of fufuraldehyde, benzaldehyde, salicyaldehyde, crotonaldehyde, cinnamaldehyde, acetylacetone or acetophenone with ethanolic solution of cyanoacyl–hydrazine. Each reaction mixture was heated under reflux on a water bath for 2–5 h in the presence of a few drops of glacial acetic acid. The precipitate was separated by filtration, washed with 5–10 mL absolute ethanol and recrystallized from ethanol and dried. The proposed formulas of the ligands are in good agreement with their analytical data, mass (table 1) and IR spectra. The ^{1}H NMR spectra of HBCH, HMCH and H_2SCH in d_6-DMSO showed signals at δ 9.68–8.70, 7.90–6.93 (multiple signals), 3.98–4.34 and 9.20–7.51 ppm assigned to the NH, aromatic, CH_2 and CH protons, respectively [16, 17]. Moreover, the spectrum of H_2SCH showed the OH proton at 11.10 ppm [16, 18].

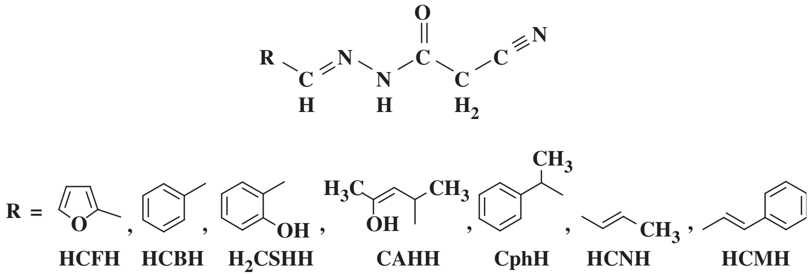

Figure 2. Chemical formulas of hydrazones.

2.2. *Synthesis of Cu(II) complexes*

The complexes were prepared by heating under reflux 1 : 1 mixture of each ligand (3 mmol) and copper acetate (3 mmol). The reaction mixture was refluxed on a water bath for 4–6 h. The precipitate was filtered off, washed with hot water, hot ethanol and diethylether and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

2.3. *Procedure for the pH-metric titration*

The experimental procedure was carried out at 25 ± 1°C. NaOH was added from a burette and the content of the titration vessel was stirred magnetically. The titration was carried out for:

(a) 2.5 mL HCl ($10^{-2}\,\mathrm{mol\,L^{-1}}$) + 1.25 mL KCl ($1.0\,\mathrm{mol\,L^{-1}}$) + 10 mL EtOH
(b) 2.5 mL HCl + 1.25 mL KCl + 0.25 mL ($10^{-2}\,\mathrm{mol\,L^{-1}}$) ligand + 9.75 mL EtOH
(c) Solution b + 0.05 mL ($10^{-2}\,\mathrm{mol\,L^{-1}}$) Cu(II) ion

The above solutions were made up to 25 mL with twice distilled water and titrated against $0.99 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ NaOH. The n_{A}^{-} is easily calculated [19] applying Irving and Rossotti equations:

$$n_{\mathrm{A}} = Y + \frac{(V_1 - V_2)([A] + [B])}{(V_0 + V_2)T_{\mathrm{L}}}$$

where Y is the ionizable proton(s) of the ligand, V_1 and V_2 are the volumes of alkali required to reach the same pH in HCl and the ligand curves, respectively, V_0 is the initial volume of the mixture, T_{L} is the ligand concentration in the initial volume, $[A]$ and $[B]$ are the concentrations of HCl and NaOH, respectively. The n^{-} and pL values were evaluated by the equations:

$$\bar{n} = \frac{(V_3 - V_2)([A] + [B])}{(V_0 + V_2)\bar{n}_A T_{\mathrm{M}}}$$

$$pL = \log\frac{1+_1 + K_1[\mathrm{H}^+]}{T_{\mathrm{L}} - \bar{n}\cdot T_{\mathrm{M}}}\cdot\frac{V_3 + V_0}{V_0} \quad \text{for monobasic ligand}$$

$$pL = \log\frac{1+_1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2}{T_{\mathrm{L}} - \bar{n}\cdot T_{\mathrm{M}}}\cdot\frac{V_3 + V_0}{V_0} \quad \text{for dibasic ligand}$$

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where V_3 is the volume of alkali required to reach the desired pH in the complex solution and T_M is the initial concentration of metal ion.

2.4. *Chemical and physical measurements*

C and H content were determined at the Microanalytical Unit of Cairo University. Copper analysis was carried out according to the standard method [20]. The infrared (KBr discs), electronic (nujol mulls and DMF solutions), ^{1}H NMR (d_6-DMSO, 200 MHz) and mass spectra were recorded on a Mattson 5000 FTIR spectrophotometer, $UV_{2\text{-}100}$ Unicam UV/Vis, Varian Gemini and Varian MAT 311 spectrometers, respectively. Thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of 10°C min^{-1} under nitrogen gas.

3. Results and discussion

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The formulas of the complexes together with their physical properties, elemental analysis and formula weights obtained from mass spectra are listed in table 2. The isolated solid complexes are stable at room temperature, non-hygroscopic and insoluble in water and most organic solvents, but easily soluble in DMF and DMSO.

3.1. *IR spectra*

Comparison of the IR spectra of ligands and their Cu(II) complexes revealed that the ligands bonded in enol form in several ways. In [Cu(CFH)(OAc)] (**1**), $[Cu(CphH)_2]H_2O$ (**5**), $[Cu(CNH)(OH)(H_2O)_3]$ (**6**) and $[Cu_2(CMH)(OH)_2(OAc)]$ (**7**), the ligands are mononegative bidentate coordinating through =N and O, shown by: (i) the disappearance of ν(NH); (ii) the shift of ν(C=N) by 16–34 cm^{-1} to lower wavenumber [17]; (iii) the appearance of a new band at 1620 cm^{-1} assigned to ν(N–N=C–O); (iv) the presence of a new band at 428–445 cm^{-1} assignable to ν(Cu–N) [18] and (v) coordination *via* enolic oxygen is indicated by the absence of ν(C=O) with simultaneous appearance of 1130–1150 and 495–500 cm^{-1} bands due to ν(C–O) and ν(Cu–O), respectively [21].

Table 2. Physical properties, analytical data and formula weights (F.W.) of the copper(II) complexes.

					Found (Calcd) (%)			F.W.	
No.	Complex	Color	Dec. p. (°C)	$\Lambda_M^{(a)}$	C	H	Cu	Found[b]	Calcd
1	[Cu(CFH)(OAc)]	Yellowish brown	>300	11.8	41.0(40.3)	3.3(3.0)	20.7(21.3)	–	298.7
2	$[Cu(CBH)(OAc)(H_2O)]$	Brown	200	17.9	43.9(44.1)	4.0(4.0)	18.8(19.4)	326.0	326.8
3	$[Cu(CSH)(C_2H_5OH)]$	Green	220	17.0	46.3(46.3)	4.8(4.5)	21.0(20.4)	312.0	311.5
4	$[Cu(CAH)(OAc)(C_2H_5OH)]$	Brown	235	34.0	40.5(41.3)	6.0(5.5)	17.7(18.2)	348.0	348.5
5	$[Cu(CphH)_2]H_2O$	Dark green	210	13.0	53.9(54.8)	4.8(4.6)	12.5(13.2)	482.0	481.9
6	$[Cu(CNH)(OH)(H_2O)_3]$	Green	290	11.8	28.7(29.6)	5.3(5.3)	22.1(22.3)	–	284.4
7	$[Cu_2(CMH)(OH)_2(OAc)]$	Olive green	270	32.6	38.1(38.9)	3.4(3.5)	29.0(29.4)	431.0	431.7

[a] In Ω^{-1} cm^2 mol^{-1}; [b] values obtained from mass spectra.

In [Cu(CBH)(OAc)(H_2O)] (**2**) and [Cu(CAH)(OAc)(C_2H_5OH)] (**4**), the ligands are mononegative tridentate *via* =N, C–O and C≡N by releasing the enolic C–OH proton. This mode of chelation was confirmed by: (i) the disappearance of ν(NH) and ν(C=O) with the appearance of ν(C–O) and ν(Cu–O) at 1120–1128 and 480–500 cm^{-1}; (ii) the cyano group as the third coordination site by the shift of its band to lower frequency (55–93 cm^{-1}); (iii) the ν(C=N) is shifted by 18–20 cm^{-1} and finally (iv) the new band at 440–435 cm^{-1} is attributed to ν(Cu–N).

In [Cu(CSH)(C_2H_5OH)] (**3**), the ligand is binegative tridentate by deprotonation of C–OH and OH and coordinating through C=N, O and C–O. The spectrum showed the disappearance of the OH band, disappearance of ν(C=O) and ν(NH) with appearance of ν(C–O) at 1227 cm^{-1}. Also, the strong band at 482 cm^{-1} is assigned to ν(Cu–O). The ν(C=N) is shifted to lower frequency with appearance of a new band at 430 cm^{-1} assignable to ν(Cu–N). The nitrile group is not altered. All the data support ONO coordination of H_2CSH (figure 3).

In **1**, **2**, **4** and **7**, the acetate coordinates in a non-bridging bidentate manner as indicated by the frequency difference ($\Delta\nu \leq 116\,cm^{-1}$) between ν_s and ν_{as} vibrations [16, 23, 24]. Finally, bands of coordinated water in **2** and **6** at 845–860 and 544–584 cm^{-1} are assigned to $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively [16, 25].

The disappearance of the C≡N band in [Cu(CNH)(OH)(H_2O)$_3$] indicates the cyano is affected by water forming $CONH_2$ or COOH [22].

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3.2. *pH-metric studies*

Deprotonation constants of the ligands and formation constants of their Cu(II) complexes were determined [26, 27]. The values of the average number of protons (n_A), the average number of ligand molecules attached per metal ion (n) and the free ligand exponent (pL) were calculated at different pH values. Plotting of n_A *versus* pH gives the proton-ligand formation constants ($\log K_1$ and/or $\log K_2$). The stability constants are calculated by half method [19] and checked by the least squares method (table 3). The data reveal that HCNH > HCAH > HCphH > HCMH > HCBH > HCFH for pK_1 values consistent with a direct relation between the electron-withdrawing character of the neighboring group and ionization, decreasing the electron density on the azomethine moiety and enhancing deprotonation. Thus, HCFH is less basic (lower $\log K$) than HCNH.

Metal-ligand stability constants of Cu(II)-ligand systems (table 3) were determined through the pL-n^- relationship. The data revealed that $\log K_1$ is higher than $\log K_2$ or $\log K_3$ for the same complex assuming that vacant sites on Cu(II) are more available for binding the first ligand than the second or the third. Overall stability constants

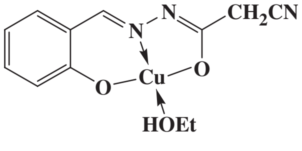

Figure 3. The proposed structure of [Cu(CSH)(C_2H_5OH)] (**3**).

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Table 3. Deprotonation constants of the ligands and the formation constants of their complexes.[a]

	H^+		Cu(II)			
Compound	pK_1	pK_2	β_1	β_2	β_3	β^*
HCFH	8.89(8.87)	–	11.05(11.25)	8.00(9.00)	5.23	24.28
HCBH	8.93(9.00)	–	9.13(8.87)	8.50	6.45(6.32)	24.08
H_2CSH	7.75(7.87)	5.20(4.96)	7.51(8.00)	5.25(5.56)	3.87(4.02)	16.63(17.58)
HCAH	11.09(10.94)	–	7.00(6.38)	6.13(5.23)	–	–
HCphH	9.92(9.93)	–	8.77(8.97)	7.12	3.15(4.46)	20.35
HCNH	11.20(11.00)	–	6.43(6.44)	– (5.89)	3.24(3.44)	– (15.77)
HCMH	9.90(9.80)	–	7.55(7.12)	6.87(6.67)	3.54	17.96

[a] values in parentheses calculated using the half method.

Table 4. Magnetic moments, electronic spectra (cm^{-1}) in DMF (nujol) of the Cu(II) complexes.

Complex	μ_{eff} (B.M.)	State	d–d Transition bands	Charge-transfer bands	Supposed structure
[Cu(CFH)(OAc)]	1.20	DMF	15775	24660	Tetrahedral
		Nujol	18380	22420	
$[Cu(CBH)(OAc)(H_2O)]$	2.19	DMF	16500	23220	Square pyramidal
		Nujol	17985	22625	
$[Cu(CSH)(C_2H_5OH)]$	1.32	DMF	15430	26040	Square planar
		Nujol	15245	29590	
$[Cu(CAH)(OAc)(C_2H_5OH)]$	1.46	DMF	17670	29940	Square pyramidal
		Nujol	16780	22830	
$[Cu(CphH)_2] \cdot H_2O$	2.05	DMF	16260	25120	Square planar
		Nujol	15110	23925	
$[Cu(CNH)(OH)(H_2O)_3]$	1.72	DMF	13330	28900	Octahedral
		Nujol	13160	22200	
$[Cu_2(CMH)(OH)_2(OAc)]$	1.46	DMF	15480	25510	Square planar
		Nujol	16560	26015	

of the Cu(II) complexes HCFH–Cu(II) > HCBH–Cu(II) > HCphH–Cu(II) > HCMH–Cu(II) > HCNH–Cu(II) reveal that HCFH has higher ability to form complexes (low pK_1).

3.3. *Electronic spectra and magnetic studies*

Magnetic moments and electronic absorption bands of the Cu(II) complexes are given in table 4. The hydrazones, except HNCH, exhibit a band at 31,250–41,320 cm^{-1} assignable to phenyl $\pi \rightarrow \pi^*$ transition which remain unchanged in the spectra of the metal complexes. The band at 24,270–30,120 cm^{-1} due to $n \rightarrow \pi^*$ is shifted to higher energy on complexation [28].

The band at 22,200–28,900 cm^{-1} in the solution spectra of the complexes may be due to LMCT [29]; studies on Cu(II)-thiosemicarbazones [21] suggested the band at 25,125–27,625 cm^{-1} be assigned to O → Cu(II) CT.

The electronic spectra of **6** in Nujol and DMF are similar, indicating that DMF has no effect on the structure of the complex. The broad band centered at 13,160–13,335 cm^{-1} is assigned to $^2E_{2g} \rightarrow {}^2T_{2g}$ in octahedral geometry [30].

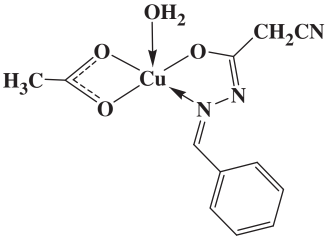

Figure 4. The proposed structure of [Cu(CBH)(OAc)(H_2O)] (**2**).

The broadening of the observed band may be attributed to the Jahn–Teller effect [13, 31]. The magnetic moment value of this complex is within the range reported for d^9-systems containing one unpaired electron and suggest Cu-L covalent bonds.

The electronic spectrum of **1** showed a band at 18380 in Nujol assigned to $^2T_2 \rightarrow {}^2E$ in tetrahedral symmetry [32]. This band is altered in DMF solution and observed at 15,775 cm^{-1}, which may be due to the coordination of DMF to occupy the fifth position forming a square-pyramid configuration.

The electronic spectra of **2** (figure 4) and **4** have a broad band centered at 16,500–17,670 cm^{-1} (DMF) and 16,780–17,985 cm^{-1} (Nujol) assigned to the d–d transition in a square-pyramid [33]; the solvent molecule takes the fifth position. The spectra of **3**, **5** and **7** have a band at 15,245–17,990 cm^{-1}, in Nujol, indicating square-planar geometry. For the square-planar complexes, three spin allowed transitions are possible, $^2B_{1g} \rightarrow {}^2A_{1g}$ $\tilde{\nu}_1(d_{x^2-y^2} \rightarrow d_z^2)$, $^2B_{1g} \rightarrow {}^2B_{2g}$ $\tilde{\nu}_2(d_{x^2-y^2} \rightarrow d_{xy})$ and $^2B_{1g} \rightarrow {}^2E_g$ $\tilde{\nu}_3(d_{x^2-y^2} \rightarrow d_{xz}, d_{yz})$, but it was impossible to resolve it into three bands [34]. The geometry is further supported by magnetic moments [34].

The magnetic moments of **1**, **3** and **4** are below the values for the spin only moment (1.73 BM), which may be attributed to copper-copper interaction [35, 36]. [Cu(CFH)(OAc)] has the lowest value.

3.4. *Mass spectra*

The recorded mass spectra for most complexes and the molecular ion peaks confirmed the proposed formula. Calculated and found molecular weights are given in table 2. As a typical example, the mass spectrum (Supplementary Material) of **3** showed successive degradation of the molecule. The first peak at $m/e = 312$ (Calcd 311.5) represents the molecular ion peak of the complex with 30.19% abundance.

3.5. *Thermal studies*

The TGA of the complexes over the temperature range 50–800°C show good agreement with the formulas suggested from analytical data (table 2). The decomposition stages, temperature range, decomposition product and the found (Calcd) weight loss% of some complexes are given in table 5.

The thermogram (Supplementary Material) of **2** is characterized by three degradation steps in the range 249–392, 393–514 and 514–722°C, the first corresponding to loss of acetate molecule; found 17.8% (Calcd 18.0%), the second from loss of coordinated

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Table 5. Thermal analyses for some complexes.

Compound, M.F. (M.Wt.)	Dissociation stages	Temperature range in TG (°C)	Weight loss found (Calcd) (%)	Decomposition assignment
[Cu(BCH)(OAc)(H_2O)],	Stage I	249–392	17.8(18.0)	OAc
$C_{12}H_{14}N_3O_3Cu$ (327.784)	Stage II	393–514	18.6(17.7)	C_7H_6
	Stage III	515–722	28.1(27.5)	$C_2H_2N + H_2O$
	Stage IV	723–800	37.4(36.6)	Residue; CN_2OCu
[Cu(SCH)C_2H_5OH],	Stage I	177–294	5.60(5.3)	OH
$C_{12}H_{15}N_3O_3Cu$ (312.474)	Stage II	295–360	14.40(14.6)	C_2H_5OH
	Stage III	361–469	42.7(41.7)	$C_7H_6 + C_2H_2N$
	Stage IV	470–800	39.4(38.2)	Residue; CN_2OCu
[Cu(CphCH)$_2$]H_2O,	Stage I	44–111	4.14(3.7)	Lattice H_2O
$C_{22}H_{24}N_6O_2Cu$ (484.012)	Stage II	112–191	9.2(8.3)	C_2H_2N
	Stage III	192–348	42.5(43.0)	$2C_8H_8$
	Stage IV	349–433	9.5(8.3)	C_2H_2N
	Stage V	434–488	37.9(36.7)	Residue; $(N_2HCO)_2Cu$
[Cu(FCH)(OAc)],	Stage I	221–293	20.7(19.7)	OAc
$C_{22}H_{24}N_6O_2Cu$ (299.724)	Stage II	294–400	29.1(30.0)	$C_4H_4O + CN$
	Stage III	400–800	49.7(48.9)	Residue; $C_3H_3N_2OCu$

water and C_2H_2N; found 18.6% (Calcd 17.7%) and C_7H_6 is evolved in the third step found 28.1% (Calcd 27.5%). The residual is CN_2OCu, found 37.4% (Calcd 36.5%). Kinetic and thermodynamic parameters for decomposition are presented in Supplementary Material.

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